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XXXIX. *A Theory concerning the Sudden Loss of the Magnetic Properties of Iron and Nickel at certain Temperatures.* By HERBERT TOMLINSON, *B.A.**

THAT very high temperatures destroy both the magnetic susceptibility of iron and its power of retaining magnetism has been known since the days of Queen Elizabeth. Thus Gilbert found that a loadstone and a piece of iron equally lost their power of affecting the magnetic needle when very hot; he also noticed that whilst the magnetic property returned to the iron after it had cooled a little, the magnetic virtue of the loadstone was altogether destroyed. Similar results were obtained by Brugmans, Boyle, Cavallo, Barlow and Bonnycastle, Christie, Ritchie, Erman, Scoresby, Seebeck, and others†. Faraday found that a steel magnet lost its permanent magnetism rather suddenly at a temperature a little under the boiling-point of almond oil (the best bitter-almond oil boils at 180° C.); it behaved like soft iron till it was raised to an orange-red heat, and then lost its magnetic susceptibility and became indifferent. The temperature at which the retentive power for permanent magnetism was lost appeared to vary in steel with the hardness and structure; in

* Read April 28, 1888.

† See Professor Chrystal's Article on Magnetism, Enc. Brit.

fragments of loadstone it was very high ; they retained their permanent magnetism until just below visible ignition in the dark (this would be somewhere about 500° C.), but lost their susceptibility at a much lower temperature than the steel. Nickel was found to lose its susceptibility about 330° C. to 340° C. (according to Becquerel about 400° C. ; according to Pouillet 350° C.). Gore has published accounts of experiments relating to the sudden loss of magnetic properties of both iron and nickel at certain temperatures*. Chrystal†, in the course of some experiments on the magnetic sounds in iron, nickel, and cobalt when traversed by an interrupted current of electricity, found evidence of sudden changes in the magnetic susceptibility of iron and nickel at certain temperatures, and gives some curves which enable us to trace the connexion between these changes and the equally curious changes of thermoelectrical power observed by Tait in iron and nickel at certain temperatures‡. Baur§ and Wassmuth‖ have also taken up the matter. According to the former, for small magnetizing forces the susceptibility of iron at first increases rapidly as the temperature increases, reaches a maximum at red-heat, and then falls suddenly to zero. For large forces the susceptibility decreases gradually up to red-heat, and then falls suddenly to a very small value. According to him, if a bar be cooled from a white heat the first traces of susceptibility are observed at a very bright red, the brighter the greater the magnetizing force. Berson¶ has published a curve showing the relation between the magnetic induction of nickel and the temperature right up to the point at which the susceptibility practically vanishes, namely, 336° C. The author** has also quite recently published similar curves for nickel, and finds that the susceptibility practically vanishes at temperatures ranging from 333° C. to 412° C. according to the strength of

* Proc. R. Soc. vol. xvii. p. 261 (1868–1869); Phil Mag. vol. xxxviii. p. 60 (1869); Phil. Mag. vol. xl. p. 175 (1870). For extracts see 'Electrician,' vol. xx. Nos. 505, 506.

† 'Nature,' vol. xxii. (1880).

‡ Heat, pp. 176–178; Trans. R.S.E. (1873).

§ Wied. *Ann.* xi. (1880).

‖ *Wien. Ber.* (1880, 1881, 1882).

¶ *Ann. de Phys. et de Chim.* vol. vii. (1886).

** Phil. Mag. vol. xxv. No. 156 (1888).

the magnetizing force, the greater the force the higher the temperature. The author, like Berson, finds the temperature at which the nickel *begins* to rapidly lose its temporary susceptibility to be 300° C. Ledeboer* has published similar curves for iron. He makes the susceptibility of iron to vanish at temperatures ranging from 750° C. to 770° C., the higher the greater the magnetizing force. The temperature at which the iron *begins* to suddenly lose its temporary magnetic susceptibility is about 680° C.

The author†, in a paper on the recalescence of iron, was led by his experiments to express a strong conviction that with iron there are two critical temperatures at which profound changes take place in the molecular architecture of the metal and at which heat becomes latent. The lower of these critical temperatures he fixes at 550° C. and the higher at 1000° C. Previously to this, but unknown to the author, Pionchon‡, by most carefully conducted calorimetric researches, had also found in iron two critical temperatures at which heat becomes latent, namely, 660°C.–720°C. and 1000° C.–1050° C. He fixes the value of the latent heat at the lower temperature at 5·3 (about $\frac{1}{15}$th of the latent heat of ice), and that at the higher temperature at 6·0. Pionchon also expresses the specific heat of iron by the following formulæ, in which γ is the specific heat at the temperature t° C.

0° C. to 660° C. $\gamma = 0{\cdot}11012 + 0{\cdot}00005066\,t + 0{\cdot}000000164\,t^2$.
660° to 720° $\gamma = 0{\cdot}57803 - 0{\cdot}002872\,t + 0{\cdot}000003585\,t^2$.
720° to 1000° $\gamma = 0{\cdot}218$.
1050° to 1200° $\gamma = 0{\cdot}19887$.

The author now believes that the lower of the two critical temperatures quoted by him previously, and deduced from his own experiments on the internal friction of iron, may be a third critical temperature§, and not, as heat first supposed, the temperature at which iron begins to suddenly lose its

* *La Lumière Electrique*, tome xxvii. no. 2.

† *Ante*, p. 10.

‡ *Ann. de Phys. et de Chim.* t. xi. (1887).

§ If this be so, there is probably another sudden change in the internal friction at 680° C.

magnetic properties, which last seems beyond a doubt to be Pionchon's first critical temperature.

In the researches of Moissan * on the allotropic modifications of iron oxide two temperatures are very conspicuous namely, 700° C. and 1000° C.

The following table, compiled from the various researches mentioned above, will show at a glance the different critical temperatures of nickel and iron which the author believes may exist† :—

Nickel.

A.	200° C. Specific heat of electricity changes sign. 200°. For low magnetizing forces the magnetic susceptibility begins to rapidly increase.
B.	300°. Magnetic susceptibility begins to very rapidly decrease. 320°. Specific heat of electricity again changes sign.

Iron.

A.	550° C. Specific heat of electricity changes sign. 550°. Internal friction of iron begins to rapidly increase.
B.	680°. Specific heat of electricity again changes sign. 680°. Magnetic susceptibility begins to very rapidly decrease. 660°–720°. Heat becomes latent.
C.	1000°. Very rapid increase of internal friction. 1000°–1050°. Heat becomes latent. About 1000° ‡. Remarkably sudden permanent yielding when under stress, and equally remarkable temporary changes when under stress or strain. Also at this temperature hot iron, which at any temperature is thermoelectrically negative to cold iron, becomes suddenly much more negative.

In the above table the author has not included certain remarkable changes which take place in the electrical con-

* *Ann. de Phys. et de Chim.* t. xxi.

† The changes taking place at A may, however, be due to approach of the critical temperature B.

‡ At least as judged by the colour.

ductivity of nickel and iron*, because these do not appear to be sufficiently near any of the above critical points. Thus Smith and MacGregor make the electrical conductivity of pure nickel foil to change suddenly at 149° C., a temperature considerably below 200° C.

Neither has the author included certain remarkable changes which have been observed to occur in the thermal expansion of steel at high temperatures †, because in the first place there are no such remarkable changes in *iron* ‡, and in the second the critical temperature in the thermal expansion of steel varies very considerably with different specimens; thus in three specimens we have abrupt changes at the temperatures 660° C., 680° C., and 725° C. The author has himself examined the thermal expansion of *iron* at different temperatures right up to and a little beyond that at which the metal showed very conspicuously sudden loss of magnetic properties without at the same time detecting anything like a sudden change in its thermal expansibility.

Evidently the critical points A and B, though occurring at a much lower temperature in nickel than in iron, correspond to similar molecular changes in the two metals, but the third critical point C in iron has apparently no corresponding point in nickel. There are at any rate no such sudden changes in nickel when under stress and strain as occur in iron.

It is, however, the critical point B in nickel and in iron which concerns the present inquiry. Why does the temporary magnetic susceptibility of both these metals diminish so rapidly that, if an iron or nickel wire be surrounded by a magnetizing solenoid always kept in action, and this again be concentric with a secondary solenoid connected with a galvanometer, a very sensible induced current can be observed at the critical temperature both on heating and cooling §? This question is a very important one, and if we can answer it

* Macfarlane, Proc. R. S. E. 1875; C. M. Smith and J. G. MacGregor, Proc. R. S. E. 1875, 1876.

† Nouel, *Génie civil*, April 1887.

‡ In the curve showing the relation between the thermal expansion of iron and the temperature there is a very slight inflection at 400° C.

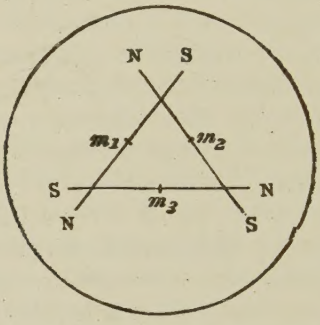
§ Even when the wire is only under the influence of the vertical component of the earth's magnetic force, the currents induced when the magnetic properties are lost or restored are quite sensible.

correctly much light will doubtless be thrown upon the nature of magnetism.

According to the author's view of the matter each molecule of iron, say, contains within itself several magnetic molecules (it may contain several hundreds or thousands).

Let the circle in fig. 1 represent a molecule of iron, and

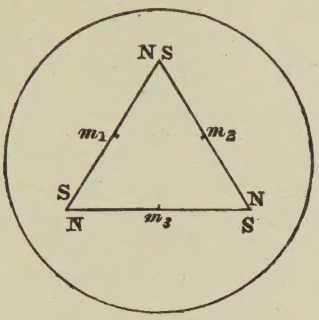
Fig. 1.



let m_1, m_2, and m_3 be the centres of the axes of three magnetic molecules. Each of these magnetic molecules, like the molecule of iron itself, is capable of motion of rotation and of motion of translation. At ordinary temperatures the magnetic molecules have their centres m_1, m_2, m_3 *so close together* that though they are endeavouring to form a *closed magnetic circuit* they are unable to do so. If now we apply a magnetizing force in any direction, each magnetic molecule will be rotated about its axis, and the whole iron molecule will be magnetized and rotated about its axis. When the magnetizing force is removed both the magnetic molecules and the iron molecules will return more or less completely to their original positions. On raising the temperature the centres of both the iron molecules and the magnetic molecules will increase their distances from each other until a certain temperature is reached, when the opposite poles of adjacent magnetic molecules will come into such close proximity that they will be able to rush together so that the system of magnetic molecules forms a close magnetic circuit, as in fig. 2. When the magnetic molecules are in this position a small magnetizing force in any direction will have no appreciable effect; but by employing larger and larger magnetizing force we may obtain

sensible evidence of magnetization, as indeed Faraday, Baur, and the author have found. The suddenness of the loss

Fig. 2.



of magnetic properties is easily comprehended when we remember the rapidity with which magnetic attractions increase as the distance between magnetic poles diminishes. We can also understand that heat at this point should become latent, for it is evident that the sudden bringing together of N and S poles, which takes place on heating, will cause a sudden expansion of m_1, m_2, and m_3. Since the action goes on *inside* the iron molecule there may be no sensible sudden increase of distance between the centre of one *iron molecule* and another, and no sensible change in the molar dimensions of the iron. This agrees with the fact ascertained by M. Nouel and the author that, at any rate in the case of annealed iron, there is no sudden change in the thermal expansibility at this critical temperature.

When the temperature, after it has been raised to the critical point, is again lowered, the centres m_1, m_2, m_3, will creep closer together again and the magnetic properties will reappear as suddenly* as they were lost.

According to the theory, it would seem that if we could make the magnetic molecules assume a sufficiently closed magnetic circuit, iron and nickel might be converted into diamagnetics. Indeed we can understand that diamagnetics may be such in consequence either of a paucity of magnetic molecules in each molecule of the substance, or from having their magnetic molecules forming nearly closed circuits.

* The suddenness of both loss and gain of magnetic susceptibility may also be conditioned by internal friction.

Again, if the temperature be raised high enough it would seem possible to partly restore the lost magnetic susceptibility; for then, by the further expansion of m_1, m_2, and m_3, the N and S poles would begin to be separated. If, therefore, such metals as bismuth are diamagnetic at ordinary temperatures, partly because their magnetic molecules form closed circuits, rise of temperature should make them more magnetic or less diamagnetic. This seems to be the case, for the experiments of Plücker and Matteucci led them to conclude that the susceptibility of diamagnetics diminishes with increase of temperature ; in the case of bismuth the decrease between ordinary temperatures and its melting-point is said to be about one sixth or more*

The following experiments were made with the apparatus which has already been described† The wire to be examined was suspended vertically in the axis of a glass tube, being clamped at its upper extremity into a brass block resting on a wooden support fitting on to the top of the tube, and provided with a terminal screw for making connexion with one pole of a battery of thirty Grove's cells. The current from this battery was employed to heat the wire and passed in or out of the latter through the intermediation of a mercury-cup, into which dipped a stout copper wire attached to a brass block clamped to the lower extremity of the wire.

Experiment I.

A piece of very soft and well-annealed iron wire, 30 cm. long and 1 mm. in diameter, was suspended in the glass tube, so that it could freely swing torsionally. The glass tube was placed inside a magnetizing solenoid, which was in turn coaxial with a secondary solenoid connected with a Thomson's reflecting-galvanometer. The magnetizing solenoid was actuated by 2 Grove's cells, which were kept in action throughout the experiment. As soon as the current from the 30 Grove's cells had heated the wire to a dull red, there was a slight deflection of the Thomson's galvanometer, indicating that the iron had suddenly lost part

* Chrystal, Enc. Brit., Art. Magnetism.
† Phil. Mag. vol. xxiv. p. 258.

of its magnetic susceptibility; then, after a pause of three or four seconds, there was a much greater deflection of the galvanometer in the same direction. Again, when the wire was allowed to cool, there was first a slight deflection of the galvanometer, indicating partial restoration of magnetic susceptibility followed immediately by a much larger deflection*. It seems likely that the interval between one deflection and the next, when the wire is being heated or is cooling, is the first of the two periods during which, according to Pionchon, heat is becoming latent. There is a similar pause, though not quite so marked, in the sudden jerk which occurs in an iron wire which has been permanently strained when the critical temperature C has been reached †, and when, according to Pionchon, heat a second time becomes latent.

Experiment II.

In this experiment an attempt was made to abolish the deflections of the Thomson's galvanometer, due to the sudden loss or restoration of the magnetic susceptibility, by torsionally oscillating the wire during the whole period of heating or cooling. But no amount of torsional oscillation availed anything.

Experiment III.

The experiments of Faraday and others, quoted previously, show that there is a temperature at which *permanent* magnetization in steel begins to be rather suddenly lost, and that this temperature is considerably lower than the temperature at which the temporary magnetic susceptibility begins to rapidly diminish. The author has also found that when a permanently twisted wire is heated it begins at a certain temperature to rapidly ‡ lose its permanent strain. It seemed, therefore, desirable to ascertain if this sudden loss of permanent molecular strain would, like permanent magnetization, take place at a lower temperature than the loss of temporary susceptibility. The iron wire in the last experiment was,

* This pause between one deflection and another has already been noticed by Mr. Newall (Phil. Mag. vol. xxiv. p. 435).

† Phil. Mag. vol. xxiv., 1887.

‡ This sudden loss of permanent strain must not be confounded with the sudden jerk which takes place at the critical temperature C.

therefore, permanently twisted through twenty revolutions and then released from torsional stress. When, on heating, a certain temperature had been reached there was a sudden untwisting of the wire, *followed after an interval of several seconds* by the usual deflection of the Thomson's galvanometer, which showed that the temporary magnetic susceptibility was beginning to disappear. This experiment was repeated at least six times with different pieces of the same kind of wire, and, invariably, with the same result—the permanent torsion, like the permanent magnetism, began to disappear suddenly at a temperature considerably below the temperature at which the temporary magnetic susceptibility began to disappear.

The contrary, however, was the case with a specimen of annealed nickel wire* of the same length as the iron but of rather less diameter. When this wire had received a few turns of permanent torsion†, and was afterwards heated, the loss of temporary magnetic susceptibility occurred at a much lower temperature than the rapid loss of permanent torsion ; whilst Berson has shown that the permanent *magnetization* of nickel resembles the permanent magnetization of iron in disappearing before the temporary susceptibility.

This experiment, therefore, shows that the temperature at which permanent magnetism begins to suddenly disappear is not the temperature at which permanent torsion begins to suddenly disappear.

XL. *On Electromotive Forces of Contact.*

By CHARLES V. BURTON, *B.Sc.*‡

THE principal object of this paper is to discuss the seats of the electromotive forces developed by the contact of conductors, and by considering the transformations of energy which occur when two insulated conductors are brought into contact, an attempt is made to give a logical demonstration of some of the views put forward. In the latter part of the paper a description is given of some experiments on the

* Containing nearly 98 per cent. of nickel

† Only two or three turns can be given before the wire breaks.

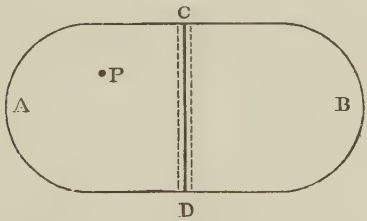
‡ Read April 28, 1888.

nature of the electrification of non-conductors by contact or friction.

When two conductors are brought into contact, an electromotive force (E) is set up between them, which drives electricity across the junction, until the difference of their potentials* has an E.M.F. equal and opposite to E. I shall assume that E is always the same so long as we keep to the same substances and the same temperature; and also that when electric equilibrium has been established each conductor is at a uniform potential throughout, except very near the junction, and that there the potential changes in general by a finite amount as we pass through a layer of very small but finite thickness, which includes the surface of separation.

Let the two conductors A and B (fig. 1) be in contact over

Fig. 1.



the surface CD, and let the difference of their potentials be finite. The potential is constant throughout the extent of A, and also throughout the extent of B, except within a very thin layer including the surface CD, which may be called the *layer of variable potential*, and where the potential may be supposed to change continuously from that of A to that of B as we pass from one side of the layer to the other. Now, consider the distribution of electricity on the system. Electric masses will be distributed on the external surfaces of A and B, but not within these surfaces, except within the layer of variable potential. Here the distribution evidently depends upon the thickness of the layer, the law of variation of

* Wherever the potential of a conductor is spoken of, the potential at any point throughout its volume is intended, and not the potential at a very near external point. I must apologise for this unusual use of the term.

potential across the layer, and the specific inductive capacity of A and B. This last quantity is evidently the true or finite specific inductive capacity, and not the apparent or infinite specific inductive capacity which conductors appear to have in ordinary electrostatic experiments; for in the latter case the electric potential energy of the layer CD would be infinite.

It is usually supposed that the contact E.M.F. between two conductors is due to some molecular action between them. And my first point is to show that this action is confined to molecules within the layer of variable potential.

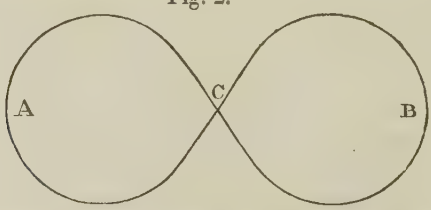
For consider a particle P (fig. 1) within the conductor A, so that all around P the potential is constant. Then if P takes part in any way in maintaining a difference of potentials between A and B, it must in turn be reacted on by the electric forces which tend to equalize the potential throughout the system. Now, the only forces tending to equalize the potential are the attractions and repulsions *inter se* of the electric masses distributed on the conductors; and the particle P being situated in a region where the potential is constant, the electric force at P is zero.

Therefore P suffers no reaction from the electric masses of the system and cannot, therefore, play any part in maintaining the difference of potential.

Hence *the molecular action which gives rise to a contact E.M.F. between two conductors is confined to the immediate neighbourhood of the junction.*

Now, suppose that two conductors A and B (fig. 2), whose

Fig. 2.



contact-difference of potentials is P, are originally at the same potential, and are then brought into contact at C. As soon as this is done an E.M.F. E (= −P) will act between A and B, and will drive electricity across the junction at C, until the difference of potentials of A and B becomes equal to P.

At the beginning of the operation, when contact first occurs, there is no E.M.F. opposed to E, so that when E drives a quantity dM of electricity across the junction, the work done is EdM. As there is no opposing E.M.F. to be overcome, the whole of this work is spent in producing heat, according to the Joule effect.

At a later stage, when the difference of potentials has become (say) p, the total E.M.F. between the conductors $=\mathrm{E}+p$; p being of course of the *opposite sign* to E. Hence, when the quantity dM crosses the junction, the work $(\mathrm{E}+p)d\mathrm{M}$ is spent in producing the Joule effect ; while the electric potential energy of the system increases by $-pd\mathrm{M}$; so that the total work done on dM by the E.M.F. E $=\mathrm{E}d\mathrm{M}$.

Hence, if in order to establish the difference of potentials P between A and B, the quantity M of electricity must cross the junction, the work done by the E.M.F. E during the operation is E.M., half this work being spent in producing the Joule effect, and half in raising the electrostatic potential energy of the system.

But the E.M.F. E is due to molecular action in the immediate neighbourhood of the junction, and, therefore, when the E.M.F. E does work by causing a displacement of electricity, a corresponding amount of molecular energy is absorbed *at the junction.*

Now, E being finite, suppose that the surface of contact at the junction C (fig. 2) is very small, and that the electrostatic capacities of the conductors are very great. Then M will be very great, and so will EM. In fact, keeping the junction as small as we please, we may increase EM indefinitely by increasing the electrostatic capacity of the system.

But, by hypothesis, the E.M.F. E will always be maintained so long as we keep to the same substances, and maintain them at the same constant temperature.

Hence, when the E.M.F. E does work, the molecular energy absorbed is of such a nature that it can be supplied in indefinite amount by a small finite junction maintained at a constant temperature.

There are only two kinds of energy which fulfil this condition : — (1) Heat ; (2) Chemical action at the junction.

First, suppose that the conductors A and B (fig. 2) are incapable of acting chemically upon one another. Then for every quantity dM of electricity which crosses the junction in the direction of the E.M.F. E, this E.M.F. does work EdM, and an equivalent amount of heat is absorbed at the junction. And, conversely, if electricity dM cross the junction in the opposite direction, work will be done against those molecular agencies at the junction which maintain the E.M.F. E, *i. e.* the work done on the E.M.F. E will appear in the form of heat.

Hence, *the true contact E.M.F. between two chemically inactive conductors is equal to their coefficient of the Peltier effect expressed in absolute measure.*

An argument sometimes advanced against this proposition is substantially as follows (I quote from Professor Lodge's paper in the Phil. Mag. for April 1885, p. 260) :—"When Q units of electricity are transmitted against a force E, work EQ is done; also when they are transmitted up a difference of potential V^1-V, work $Q(V^1-V)$ is done; but in an open circuit containing an electromotive junction, V^1-V is produced by and is equal to E. Hence, at an electromotive junction no work need be done by a current; in other words, the existence or non-existence of a Peltier effect has nothing to do with the existence or non-existence of a local E.M.F."*

But although on an open circuit, there are two equal and opposite E.M.F.'s at the junction, and consequently there is no resistance to the flow of electricity in either direction, still the E.M.F. which acts in the direction of the flow *will do work upon the opposing E.M.F.*

A mechanical example may make this clearer. If a particle be acted upon by two equal and opposite forces, each of one dyne, the smallest possible force will be able to displace the particle in any direction; but if the particle be displaced one centimetre in the direction of one of the dyne-forces, this force will do just one erg of work upon the other force.

Now, at the junction between two chemically inactive conductors, the two E.M.F.'s are (1) an E.M.F. E due to a tendency to absorption of heat-energy at the junction, and transformation of the absorbed energy into electrical energy

* Professor Lodge refutes this by a hydrostatic analogy.

by displacement of electricity across the junction, and (2) an E.M.F. P ($=-E$) due to difference of potentials between the conductors.

Hence, if electricity M cross the junction in the direction of the E.M.F. E, heat-energy EM is absorbed in order to drive the quantity M up the step of potential; while if electricity M cross the junction in the opposite direction, energy EM will be given out in descending the step of potential and will appear in the form of heat.

Returning now to the consideration of the conductors A and B (fig. 2), suppose that they are capable of acting chemically upon one another. In this case the energy required to establish the difference of potentials between A and B may be supplied at the junction either in the form of heat absorbed there or chemical action taking place. For the sake of simplicity let the Peltier E.M.F. be zero, so that we have only to deal with a chemical E.M.F. It will also be simplest to consider one of the conductors to be a solid and the other a liquid, so that any chemical action which may take place will not modify the nature of the subtances in contact.

For every quantity M of electricity which crosses the junction in the direction of the E.M.F. chemical energy EM will be absorbed, *i. e.* an amount of chemical action proportional to M will take place.

This is in accordance with Faraday's Electrolytic Law.

Professor Lodge considers that the E.M.F. between chemically active substances is due to a *tendency* to chemical action. But mere tendency to chemical action at a finite junction could not be the source of an indefinite amount of energy, and could not, therefore, account for the phenomena in the case discussed above. There must be actual chemical action. It appears in fact (excluding all idea of a Peltier E.M.F.) that when two chemically active conductors are brought into contact, electricity in general crosses the junction, and establishes a difference of potential between them, and *the amount of chemical action which takes place is precisely the equivalent of the electricity which crosses the junction determined in accordance with Faraday's Electrolytic Law.*

Let K = number of absolute units of energy evolved when one gram of (say) the substance A enters into the kind of combination which takes place in the case considered.

Let k=number of grams of A which enters into combination per unit flow of electricity.

Then for every unit of electricity which crosses the junction, E units of chemical energy are absorbed ; $\therefore$ E/K grams of A are dissolved.

$$\therefore \text{E/K}=k \text{ or } \text{E}=k\text{K}.$$

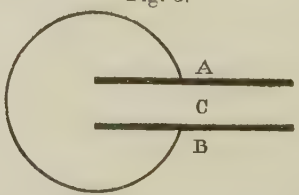
That is, *the E.M.F. is equal to the energy of combination of one electrochemical equivalent.*

Of course this is only the case where all the energy of the chemical action is converted into electrical energy ; as in the case of pure zinc dipped in dilute sulphuric acid. From this it follows that in the case of the typical cell, for instance, where pure zinc and pure copper are immersed in dilute sulphuric acid, the principal E.M.F is at the contact of the zinc and acid, an opposing E.M.F. being set up at the contact of acid and copper.

If we construct a cell consisting of zinc and carbon dipping in dilute H_2SO_4, there will be no power of chemical action at the liquid-carbon junction, so that the only E.M.F. there is a Peltier E.M.F. Neglecting Peltier E.M.F.'s altogether, the E.M.F. of such a cell would be equal to that of the zinc-liquid junction.

The apparent contact E.M.F.'s of metals, as measured in air, must be due chiefly to the air-metal contacts, since a metal-metal contact can only be the seat of a Peltier E.M.F. It also appears that if the apparent E.M.F. between two metals were measured inductively in some chemically inactive gas (or liquid), the result would be the sum of three Peltier E.M.F.'s, and would probably be small. There even seems to be some reason for supposing it to be zero.

Fig. 3.



For consider a circuit consisting of two metals A and B (fig. 3) and an inert gas C, all at the same temperature. Suppose that there is on the whole a finite E.M.F. in the

circuit ACBA, *i. e.* that the potential of the gas C varies as we pass from the plate A to the plate B. Now, it is evident that if the gas C has any trace of conductivity, or any power whatever of equalizing potentials by convection, a feeble current will flow continuously around the circuit ACBA, and will derive its energy from absorption of heat at one or more of the junctions, which would be a violation of the Second Law of Thermodynamics. If the metal A were furnished with points as fine as possible, and if these points were brought within an extremely small distance of B, they would greatly favour any conductive or convective tendency that might exist; and if by such an arrangement a convective discharge of only one molecule of electricity in a century were established, it would constitute a violation of the Second Law of Thermodynamics.

If we admit that in an inert gas C the difference of potential between the layers in contact with A and B is finite, we must assume that the gas is an *absolutely perfect insulator* for such an E.M.F. Even if this property is assumed it does not follow that Volta's Law is inapplicable to the case of gases and metals.

I have endeavoured to show how a Peltier E.M.F. depends on a tendency to absorb heat-energy and convert it into electrical energy. Now from the law of successive contacts of chemically inactive conductors, it is evident that, the temperature being fixed, we can connect with each substance a constant (called its "Peltier-constant") such that the E.M.F. between any two inactive conductors is equal to the difference of their respective constants, which is only another way of stating Volta's Law.

Now it seems not unlikely that the Peltier constant of a given conducting substance, at a given temperature, depends only on the size, form, &c. of its molecules, and the nature of their heat-motion; and, if so, each non-conductor should also have its Peltier constant, since the conditions are essentially the same in the two cases.

Thus the law of successive contacts might hold for chemically inactive non-conductors as well as for conductors.

It might even be that the law is universally true so far as Peltier E.M.F.'s only are concerned; but of course these are only speculations.

The following are some analogous properties of Peltier E.M.F.'s and chemical E.M.F.'s arranged respectively in parallel columns :—

Peltier E.M.F.	Chemical E.M.F.
1*a*. When the two substances originally at the same potential are brought into contact an E.M.F. E_1 is established across the junction; this E.M.F. continues to displace electricity across the junction until the E.M.F. due to difference of potentials $= -E_1$	1*b*. When the two substances originally at the same potential are brought into contact an E.M.F. E_2 is established across the junction; this E.M.F. continues to displace electricity across the junction until the E.M.F. due to difference of potentials $= -E_2$.
2*a*. The energy required to establish the difference of potentials is supplied by heat absorbed at the junction.	2*b*. The energy required to establish the difference of potentials is supplied by chemical action taking place at the junction.
3*a*. For every quantity M of electricity which crosses the junction in the direction of the E.M.F. E_1, a quantity of heat-energy E_1M is absorbed at the junction.	3*b*. For every quantity M of electricity which crosses the junction in the direction of the E.M.F. E_2, a quantity of chemical energy E_2M is absorbed at the junction.
4*a*. For every quantity M of electricity which crosses the junction against the E.M.F. E_1, heat-energy E_1M is given out at the junction.	4*b*. For every quantity M of electricity which crosses the junction against the E.M.F. E_2, energy E_2M is given out at the junction, and appears either as chemical-energy (electrolysis) or as heat.
5*a*. The heat absorbed at the junction during the operation (1*a*) is the equivalent of the electricity which crosses the junction, determined in accordance with the laws of the Peltier effect.	5*b*. The chemical action at the junction during the operation (1*b*) is the equivalent of the electricity which crosses the junction, determined in accordance with Faraday's Electrolytic Law.

Sir W. Thomson has deduced a lower limit to the size of atoms by a method which is well known. Professor Lodge points out that the limit cannot be assigned with certainty, until the true contact-difference of potentials of the substances concerned is known. But there is another point to be considered. The method assumes that there is a kind of affinity between the molecules of the two metals concerned ; that on contact being made, this affinity gives rise to an E.M.F. which establishes a difference of potential, the necessary energy being furnished by the partial satisfaction of the said

affinity. The method further assumes that when the metals are fused together it is this same affinity which, being satisfied as completely as possible, gives rise to an evolution of heat. But if (as appears from what precedes) the energy required to produce the difference of potentials is supplied by absorption of heat at the junction, and if the contact E.M.F. is due to a tendency to convert heat-energy into electrical energy, then the heat evolved on fusing the metals together can have no direct connexion with E.M.F.'s of contact, and the method would not apply to the case of two metals.

It would, however, obviously apply where the E.M.F. was due to chemical affinity, as in the case of zinc and oxygen proposed by Professor Lodge (Phil. Mag. May 1885, p. 363). In all these investigations the electrostatic capacities are calculated on the assumption that the specific inductive capacity of the conductors is unity. I have not been able to find any experimental justification for this assumption.

Electrification of Non-conductors.

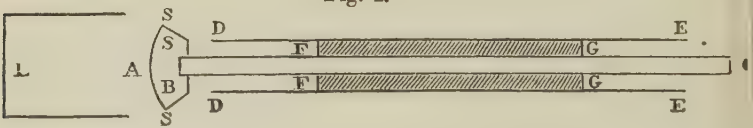
When two non-conductors are brought into contact, there are other sources of energy which may cause electrification. For if the bringing of two free surfaces into contact, or the striking or rubbing of the bodies together, should give rise to electrification, the charges so produced would remain separated, owing to the insulating properties of the substances. This source of electrification is absent in conductors, as any electrification produced between them by sudden violence would be destroyed by conduction, the final difference of potentials between the bodies being always that due to a definite contact E.M.F.

The difference between the two cases may be illustrated by considering the case of a spring. If a force be applied to the spring a definite compression will ensue, supposing that there is no friction ; and if by any temporary impulse the compression be increased or diminished, it will regain its former value when the impulse ceases to act. The inverse of the strength of the spring represents the capacity of the system, the force compressing the spring the E.M.F. of contact, the distance through which the spring is compressed the quantity of electricity displaced, and the potential energy of

the compressed spring the electrostatic potential energy of the two conductors.

If we suppose compression or extension of the spring to be accompanied by friction, a compression effected by a sudden shock will be maintained. This illustrates what perhaps takes place with non-conductors. In order to test which view is the more correct, I have made a few experiments on the electrification of glass and ebonite when dipped into mercury. This method of experimenting seemed to offer several advantages. The mercury being permanently connected to earth was always at a known potential (zero), and it was only necessary to measure the charge of the ebonite or glass. Then, again, contact was obtained over the whole surface submerged, with very little mechanical violence when desired; and the conditions of contact could be considerably varied by using more or less suddenness and violence and longer or shorter duration of contact.

Fig. 4.



The ebonite or glass employed consisted of a small circular slab S (fig. 4) with a convex surface A, which was attached to one end of a rod BC of the same material. This rod was encased in a brass tube DE, inside which it was fastened by means of packing FG. The length BF of ebonite or glass served to insulate the slab A. In the case of the glass the length BF was varnished. The charge on A was measured by means of the conductor L connected to a Thomson electrometer. A was placed near to L, which was put to earth and then insulated. On withdrawing A, a deflection was produced proportional to the charge on A. The movement of A was controlled by making the tube DE slide in metal bearings between fixed stops. The tube DE being of metal, no electrification was produced by friction in the bearings. The following results were obtained:—

(a) *Ebonite and Mercury.*	DEFLECTION.
Dipped once and quickly withdrawn	+10 to +12
„ „ very quickly withdrawn . .	+15
„ for 10″ quickly withdrawn	+ 7 to +15
„ „ 15″ „ „	+ 6 to +10
„ „ 30″ „ „	+ 6 to +13
„ „ 60″ „ „	+ 5 to + 9
30 rapid splashes in the mercury	− 6
50 not very rapid splashes in the mercury .	+ 7
100 rapid „ „ „ .	−11
200 „ „ „ „ .	−10

(b) *Glass and Mercury.*	DEFLECTION.
Dipped once quietly	+ 6 to +10
20 rapid splashes	− 7
50 „ „	− 1
60 „ „	− 6
90 „ „	+ 4
100 „ „	− 3

The above results, it will be seen, are very irregular, owing no doubt to the fact that all the circumstances of contact could not be accurately known. These irregularities, and especially the variable sign of the electrification, make it clear that the effects are not due to a true and definite contact E.M.F., but are dependent in some degree on the manner in which the surfaces are brought together and separated. The experiment of Canton in 1753 (where the rough and polished parts of a glass tube became oppositely electrified when rubbed with the same cloth) seems to point in the same direction.

Professors Ayrton, Schuster, S. P. Thompson, and J. Perry discussed the points raised, and it was considered that direct experiment on contact electromotive force in a very perfect vacuum could alone decide the question.

This experiment seems almost as impracticable as a direct measurement of the size of a molecule. Yet the two questions may be equally capable of solution by inductive reasoning. The question is whether the reasoning given above is or is not conclusive.—C. V. B.

XLI. *On Magnetic Lag.*

By Thomas H. Blakesley, *M.A.**

In bringing my views on Transformers before the Physical Society it is my desire to emphasize :—

(1) How the magnetic lag, if it exist, may be measured by employing dynamometers of low resistance.

(2) That the magnetic lag has a real existence.

(3) That the magnetic lag necessarily accompanies an absorption of work involved in the reversal of polarity in the iron, and how this may be measured.

(4) The points in the general argument where scientific facts are wanting, and the direction which investigation should take to meet this want.

The possibility of the existence of a magnetic lag renders the problem a different one from that of two coils acting and reacting upon themselves by means of mutual and self-induction, whose coefficients, being geometrical, are constant.

For the latter problem I gave in the year 1885 a complete solution, but I pointed out that the completeness of the result rested upon the absence of anything in the nature of hysteresis (a word not then in use) or work done in the field.

The following year Mr. George Forbes, F.R.S., gave what should have been (but for the very poor reporting of the Society of Arts' Journal) a solution of the "secondary generator" problem, treating it as a case of two coils, assuming that "the magnetism of the core varies as the sum of the currents in the two coils;" and the same gentleman has treated the subject again in a recent paper before the Society of Telegraph-Engineers and Electricians, in which he makes the same assumption, and says, referring to the harmonic functions which he attributes to the electrical and magnetic quantities involved, that the existence of magnetic hysteresis would cause departure from the harmonic character, but that, being insignificant so long as the magnetic induction in the iron is not high, its consideration may be omitted ; statements which seem rather to evade than to overcome the difficulty.

* Read May 12, 1888.

Mr. Gisbert Kapp, who has done so much good work in the practical development of transformers, also, in my opinion, makes the same assumption, that the state of magnetization in the core coincides with the magnetic stress resulting from compounding the stresses derived from the two coils.

In the view I shall put forward I shall assume :—

(1) That the variations are harmonic.

(2) That the only induction in the secondary coil is derived from the core, and is therefore, as regards phase, in quadrature with the magnetization. As the current in the secondary coil will be considered as producing one of the components of the stress producing magnetization, itself reacting upon the coil, the necessity of introducing a special E.M.F. of self-induction is obviated.

(3) That each turn in either coil embraces the same number of magnetic lines.

I shall also make use of the following symbols :—

E, the maximum electromotive force of the machine ;

I_1, the maximum value of the current in the primary circuit ;

I_2, the maximum value of the current in the secondary circuit ;

$\pi - \theta$, the angle of phase-difference between the currents ;

m, the number of turns of wire in the primary coil ;

n, " " " secondary coil ;

ϕ, the angle of magnetic lag ;

r_1, the resistance in the primary circuit ;

r_2, " " secondary circuit ;

α_1, α_2 are the readings of two dynamometers placed respectively in the primary and secondary circuits, their constants being A and B, so that $\frac{I_1^2}{2} = A\alpha_1$, $\frac{I_2^2}{2} = B\alpha_2$;

α_3 is the reading of a dynamometer one of whose coils is in the primary, the other in the secondary circuit. Its constant is C.

M is the maximum magnetization.

The magnetic stress produced by each coil is proportional to the current in that coil multiplied by the number of turns in the coil, and is here taken to be that product, called very

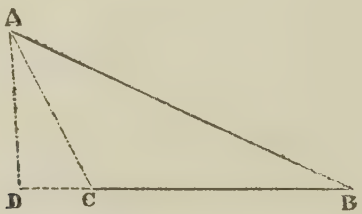
often the ampere-turns. Its maximum value in the primary coil is mI_1 and in the secondary coil it is nI_2.

Now the observations on the dynamometers A and B furnish us with a knowledge of I_1 and I_2 in any case; and m and n are details of the construction of the transformer. Thus we are in possession of the two quantities mI_1 and nI_2.

But the three dynamometer observations enable us to determine the angle of phase-difference between the currents, as I have elsewhere explained :—

$$\cos\theta = \frac{C\alpha_3}{\sqrt{A\alpha_1 B\alpha_2}} \quad \text{for } C\alpha_3 = \frac{I_1 I_2 \cos\theta}{2}.$$

We are therefore in possession of the two components of the magnetic stress and of the angle between them. Hence we are virtually in possession of the whole magnetic stress, and its phase relatively to its components. If the resultant is in quadrature with that component which results from the current in the secondary coil, it is in the same phase as the magnetization, which is in quadrature with that component; but not unless this is the case.



Let the line A B represent mI_1 or the magnetic stress in the primary circuit, and let B C represent the magnetic stress in the secondary, and let A B C be the angle θ, found as above. Then A C is the resultant magnetic stress.

But the magnetization is in quadrature with B C. Draw A D at right angles to B C. Then C A D represents the magnetic lag, which is seen to vanish if A C B is a right angle. The condition of the existence of lag is therefore that

$$CB < \dot{A}B\cos\theta,$$

which in terms of the dynamometer observations is

$$n\sqrt{2\mathrm{B}\alpha_2} < m\sqrt{2\mathrm{A}\alpha_1}\,\frac{\mathrm{C}\alpha_3}{\sqrt{\mathrm{A}\alpha_1\,\mathrm{B}\alpha_2}},$$

or

$$\mathrm{B}\alpha_2 < \frac{m}{n}\,\mathrm{C}\alpha_3.$$

The observation on the dynamometer in the primary is seen to be eliminated. Thus this question can be tested with two dynamometers only. The amount of lag is represented by the angle CAD. We can easily express its tangent in terms of the three dynamometer observations.

$$\tan\phi = \frac{\mathrm{CD}}{\mathrm{DA}} = \frac{\mathrm{DB}-\mathrm{BC}}{\mathrm{AB}\sin\theta} = \frac{\dfrac{\mathrm{DB}}{\mathrm{AB}} - \dfrac{\mathrm{BC}}{\mathrm{AB}}}{\sqrt{1-\cos^2\theta}}$$

$$= \frac{\cos\theta - \dfrac{n\mathrm{I}_2}{m\mathrm{I}_1}}{\sqrt{1-\cos^2\theta}}$$

$$= \frac{\dfrac{\mathrm{C}\alpha_3}{\sqrt{\mathrm{A}\alpha_1\,\mathrm{B}\alpha_2}} - \dfrac{n}{m}\sqrt{\dfrac{\mathrm{B}\alpha_2}{\mathrm{A}\alpha_1}}}{\sqrt{1-\dfrac{\mathrm{C}^2\alpha_3{}^2}{\mathrm{A}\alpha_1\mathrm{B}\alpha_2}}}$$

$$= \frac{\mathrm{C}\alpha_3 - \dfrac{n}{m}\mathrm{B}\alpha_2}{\sqrt{\mathrm{A}\alpha_1\,\mathrm{B}\alpha_2 - \mathrm{C}^2\alpha_3{}^2}}.$$

Thus the angle of magnetic lag, if it exist, can be detected with two dynamometers and measured with three.

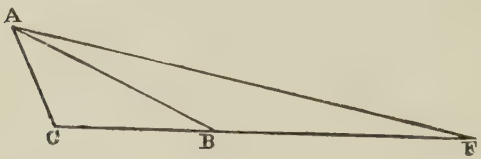
In dealing yet further with the results furnished by the observations, we must remember that the waxing magnetism has the same inductive effect in producing E.M.F. in each turn of the coils of the two circuits. But we can, from the observation of dynamometer B, say what that E.M.F. per turn is. The whole E.M.F. in the secondary coil is $\mathrm{I}_2 r_2$, consequently the E.M.F. per turn is $\dfrac{\mathrm{I}_2 r_2}{n}$. Therefore in the primary the total E.M.F. arising from magnetic induction is $m\dfrac{\mathrm{I}_2 r_2}{n}$.

The current arising from the same source is $\dfrac{m\mathrm{I}_2}{n}\dfrac{r_2}{r_1}$ and the magnetizing stress on this account is $\dfrac{m^2}{n}\dfrac{\mathrm{I}_2 r_2}{r_1}$, which must be

looked upon as one of the components of the whole magnetizing stress due to the primary current; and this component is in the same phase as the magnetizing stress in the secondary.

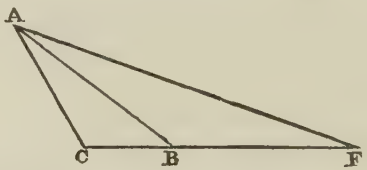
Hence, returning to the figure, if we produce CB to F so that $CB : BF :: nI_2 : \frac{m^2}{n}\frac{I_2 r_2}{r_1}$,

$$:: 1 : \frac{m^2}{n^2}\frac{r_2}{r_1}.$$



FB is one of the components of AB.

The other component (*i. e.* that arising from the machine's proper electromotive force) is AF. Hence $AF = m\frac{E}{r_1}$.



It follows that the electromotive force E, which the machine is exerting, may be thus determined by means of the dynamometer observations.

$$AF^2 = AB^2 + BF^2 + 2AB\ BF \cos ABC,$$

$$\frac{m^2E^2}{r_1^2} = m^2I_1^2 + \left(\frac{m^2}{n^2}\frac{r_2}{r_1}\right)^2 n^2I_2^2 + 2mI_1\frac{m^2}{n^2}\frac{r_2}{r_1}nI_2\cos\theta,$$

$$\therefore\ E^2 = r_1^2I_1^2 + r_2^2I_2^2\frac{m^2}{n^2} + 2r_1r_2\frac{m}{n}I_1I_2\cos\theta,$$

$$= r_1^2\,2A\alpha_1 + \frac{m^2}{n^2}r_2^2\,2B\alpha_2 + 4r_1r_2\frac{m}{n}C\alpha_3,$$

$$= 2\left\{r_1^2A\alpha_1 + r_2^2\frac{m^2}{n^2}B\alpha_2 + 2r_1r_2\frac{m}{n}C\alpha_3\right\}.$$

Another interesting magnitude is AC, or the total impressed magnetic force.

$$\begin{aligned} AC^2 &= AB^2 + BC^2 - 2AB\ BC\cos\theta, \\ &= m^2 I_1^2 + n^2 I_2^2 - 2mn I_1 I_2 \cos\theta, \\ &= 2m^2 A\alpha_1 + 2n^2 B\alpha_2 - 4mn C\alpha_3, \\ &= 2\{m^2 A\alpha_1 + n^2 B\alpha_2 - 2mn C\alpha_3\}. \end{aligned}$$

By means of this we may calculate what current should be passed through the primary circuit, the secondary being open, to produce the same state in the core.

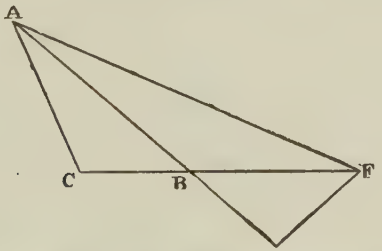
But perhaps the most interesting point to men of science and to civil engineers is the question of power. We may approach it thus perhaps in the simplest way.

By dropping a perpendicular from F upon AB produced we easily see that

$$AF\cos BAF = BF\cos ABC + AB.$$

Multiplying through by AB we have

$$AF\ AB\cos BAF = AB\ BF\cos ABC + AB^2.$$



Substituting the electric quantities for the geometrical,

$$\frac{mE}{r_1} m I_1 \cos BAF = m I_1 \frac{m^2}{n^2}\frac{r_2}{r_1} n I_2 \cos\theta + m^2 I_1^2 ;$$

multiply through by $\frac{r_1}{2m^2}$

$$\frac{E I_1 \cos BAF}{2} = r_2 \frac{m}{n} \frac{I_1 I_2 \cos\theta}{2} + \frac{r_1 I_1^2}{2}.$$

But the term on the left is the expression for the total power, and those on the right hand may be expressed in terms of the dynamometer observations.

Thus the total power

$$= r_1 A\alpha_1 + r_2 \frac{m}{n} C\alpha_3.$$

The first term here is obviously the power at work heating the primary coil.

$r_2 B\alpha_2$ is as obviously the power heating the secondary coil.

If, therefore, we write the total power

$$= r_1 A\alpha_1 + r_2 B\alpha_2 + r_2 \left\{ \frac{m}{n} C\alpha_3 - B\alpha_2 \right\},$$

we see that the power involved with the magnetic lag is

$$r_2 \left\{ \frac{m}{n} C\alpha_3 - B\alpha_2 \right\},$$

the form showing that it disappears if the lag does so.

Thus we are led to the conclusion that a magnetic lag involves a loss of power, and any loss of power due to molecular action in the core taking place in the course of the alternations of magnetization must necessarily produce lag.

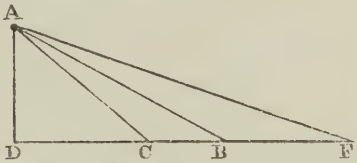
Now if the changing magnetization does work it must do it against a force, and this force must be of the character which of itself would produce magnetization, *i. e.* magnetic force. Just as when a body moving in a medium does work in the medium, it does so by calling into being, or inducing, a force, viz. friction; force being that sort of magnitude which acting upon a body produces motion.

By analogy alone, therefore, we may infer that when changing magnetization is a continuous source of absorbed work, the changing magnetization induces what would itself produce magnetization, that is an induced stress acting in opposition to the direction of the change in the magnetization.

This may perhaps be allowed; but it may be urged that there is plenty of magnetic stress already, impressed by the currents; why should not the changing magnetization work on this? The answer to this objection is that if there be no other stress but that impressed from outside, then the phase of the magnetization will be in the same phase, and *therefore the increase of magnetization* will be in quadrature with the stress, and hence no work will be continuously absorbed. For though through some phases work may be done in such a case, this is always recoverable and recovered in a complete period; a proposition which I have stated and proved in my papers upon Alternating Currents in 1885.

I apprehend, therefore, that besides the stresses AB BC we have another induced stress in quadrature with the magnetization, because called into being by its increase, and therefore in the same phase as FB or BC.

Let BC, therefore, be produced until it meets in D the line AD drawn at right angles to BC.



Then AD will be the effective magnetic stress, *i. e.* that magnetic stress which, maintained with a *steady* current, will produce the actual magnetization; hence, if M is the maximum magnetization,

$$\frac{4\pi AD}{\rho} = M,$$

where ρ is called the magnetic resistance. Thus

$$AD = \frac{M\rho}{4\pi}.$$

If 2T is the period of alternation, $\frac{\pi M}{T}$ is the maximum rate of increase of M. If

$$N\frac{\pi M}{T} = DC,$$

N may be called the coefficient of magnetic self-induction.

Under the exigencies of a certain temporary nomenclature CD might be called the Foucault-Ampere turns existing in the core itself.

Substituting for M in terms of AD,

$$DC = \frac{N\pi}{T}\frac{4\pi AD}{\rho},$$

or

$$\frac{DC}{AD} = \tan\phi = \left\{\frac{4\pi^2}{T\rho}\right\}N.$$

I have explained above how $\tan\phi$ may be obtained from the dynamometer observations. We may therefore employ this formula for the determination of the value and constancy of N, if we can rely upon the values of T obtained by observation at the time, and of ρ known otherwise.

The constancy of ρ obtains so long as magnetization can keep pace with magnetic stress. These conditions are fairly well understood, and AD must not exceed the stress representing the limiting one. Thus it will be well to know AD,

$$\begin{aligned} \mathrm{AD} = \mathrm{AB}\sin\theta &= m\mathrm{I}_1\sqrt{1-\cos^2\theta}, \\ &= m\sqrt{2\mathrm{A}\alpha_1}\sqrt{1-\frac{\mathrm{C}^2\alpha_3{}^2}{\mathrm{A}\alpha_1\mathrm{B}\alpha_2}}, \\ &= \sqrt{2}.m.\frac{\sqrt{\mathrm{A}\alpha_1\mathrm{B}\alpha_2-\mathrm{C}^2\alpha_3{}^2}}{\sqrt{\mathrm{B}\alpha^2}}. \end{aligned}$$

I think, therefore, experiment should move in the following direction. The constancy or the reverse of N under varying speeds should be first determined by experiments with currents so small or coils so few that the magnetic resistance ρ may be safely assumed constant. For this purpose it would be necessary to employ some speed-indicator.

Professor Forbes, F.R.S., in his paper upon transformers, already quoted, says that the existence of hysteresis would cause a departure from the harmonic character of the motion, but that the effects are small and negligible.

If N, however great, remains constant, the harmonic character of the variation is maintained. But if experience showed that induced stress varies as the square or higher power of the rate of change of magnetization, then indeed a serious modification would take place, and this would be likely if the neighbourhood of saturation were reached.

In the foregoing investigation I have represented *magnetic stress* as of the order *Current*, and the formulæ I have introduced hitherto will bear this convenient form of expression; but strictly speaking it is of the order *Field*, and when we wish to settle the dimensions of N we must take this into account. The M of the work is really of the order Moment or $[l^{\frac{5}{2}}t^{-1}m^{\frac{1}{2}}]$. Now the rate of increase of Moment multiplied into N is equal to Field or $[l^{-\frac{1}{2}}t^{-1}m^{\frac{1}{2}}]$;

$$\therefore \mathrm{N}\frac{[l^{\frac{5}{2}}t^{-1}m^{\frac{1}{2}}]}{t} = [l^{-\frac{1}{2}}t^{-1}m^{\frac{1}{2}}]$$

$$\therefore \mathrm{N} = [l^{-3}t].$$

The actual experiments, which I now bring to the notice of the Society, were carried out at the works of Messrs. Nalder, Brothers & Co., of Westminster, and I am greatly indebted to these gentlemen themselves, and to Mr. Crawley and Mr. Mott for their assistance in making them, for they freely placed their steam-power, their electrical power, and their intellectual power at my disposal.

These experiments had no other object than to test the question of the existence of magnetic lag by dynamometers, and to measure the angle of lag.

The machine employed and the transformer were of the Kapp forms. The numbers of turns of wire in the two coils had been ascertained for me by Mr. Crawley. They were 100 and 12 respectively.

No. of Experiment.	$A\alpha_1 = \frac{I_1^2}{2}$.	$B\alpha_2 = \frac{I_2^2}{2}$.	$C\alpha_3$.	$\frac{m}{n} C\alpha_3$.	θ.	ϕ.	$\sqrt{A\alpha_1} \sin\theta$.
1.	33·29	52·65	10·37	86·46	75° 40′	5° 43′	5·590
2.	34·43	59·74	11·50	95·83	75 19	5 38	5·676
3.	37·09	92·14	17·34	144·50	72 45	6 25	5·816
4.	70·38	86·06	17·43	145·22	77 4	5 21	8·176
5.	81·17	81·00	17·21	143·42	77 45	5 24	8·804
6.	84·97	29·03	7·83	65·26	80 56	5 4	9·103
7.	8·21	101·59	14·31	119·26	60 17	4 50	2·488

No. of Experiment.	r_1.	r_2.	$\frac{I_1}{2} r_1$.	$\frac{I_2^2}{2} r_2$.	Power of internal magnetic work $\equiv$ H.	$\frac{H}{A\alpha_1 \sin^2\theta}$.
1.	2·01	2·51	66·91	132·15	84·96	2·72
2.	,,	2·36	69·20	140·99	85·17	2·64
3.	,,	1·96	74·55	180·59	102·63	3·03
4.	,,	...	141·46			
5.	,,	2·87	163·15	232·47	179·15	2·31
6.	,,	4·77	170·79	138·47	172·82	2·09
7.	,,	0·72	16·50	73·14	12·73	2·06

Considering the considerable differences in the relations of the currents, the constancy of the angle of lag appears to me to point to a simple law connecting it with the magnetization.

There was no very accurate speed-indicator employed, and the speed was approximately the same in the first six experiments. In the seventh experiment the speed was purposely much diminished, by about one third of that in the former cases, and in this experiment alone does the lag appear at less than 5°.

XLII. *Note on the Governing of Electromotors.*

By W. E. Ayrton *and* John Perry*.

In 1882 a method was brought forward by us for governing electromotors, so that their speed should not be varied by an alteration in the load. The method, which was worked out theoretically and experimentally, was based on the combination of a motor, which converted electric energy into mechanical energy, with a brake dynamo, which reconverted the surplus mechanical energy into electric energy. After passing through various stages the arrangement finally resolved itself into an electromotor having the field-magnet wound with a shunt- and a series-coil, the coils being so connected with the rest of the circuit that the currents passed round them in opposite directions. Hence the magnetic excitation of the field-magnet was produced by the difference in the number of ampere-turns of the two circuits passing round it.

This method of governing motors, which has since 1882 been reinvented in France by M. Deprez, in America by Mr. Sprague, and which has formed the subject of an exhaustive series of experiments carried out in Germany by Dr. Fröhlich, answers well and produces a very fair constancy of speed for very considerable variations of the load. But it has a very decided defect, arising from the fact that since the series- and shunt-coils on the field-magnet oppose one another's action, the magnetization cannot be produced as economically as if there were no such differential action. Mainly on this account we have not developed our method

* Read May 26, 1888.

of governing as energetically as we might otherwise have been led to do.

In our original investigation of the subject we considered the conditions for governing motors either when a constant PD. (potential-difference) or when a constant current was supplied, and in both cases the practical solution we arrived at was a differential winding of the field-magnet. But we have since noticed that, in the case of the supply conditions being constant current, our original equations could be differently interpreted, and that the demagnetizing series could be dispensed with. Consequently a motor for constant current can be made to go at a constant speed with a varying load, and in addition to have the high efficiency of a well-made dynamo.

We shall for the general consideration of the problem use the simplest equations for a motor, disregarding saturation, as we did in our original paper, since, although the results so obtained for critical speed, &c., cannot be used directly without correction in actual practice, these equations are sufficiently accurate to show whether or not a certain combination is a possible or an impossible one for obtaining a certain required result.

If E be the back E.M.F. in the armature of a motor at a speed of n revolutions, if p be a term depending on the permanent magnetism in the iron of the field-magnet, S the current passing round the series-coil, and Z the current round the shunt-coil, we have

$$\mathrm{E}=n(p\pm q\,\mathrm{S}\pm t\mathrm{Z}). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The signs + or − in the two terms being used as the series- and the shunt-currents respectively help or oppose the permanent magnetism.

If s and z be the resistances of the series- and shunt-coils respectively, a the resistance of the armature, and A the current round the armature, we have in the case of what has been called a short shunt (fig. 1),

$$\mathrm{E}=\mathrm{Z}z-\mathrm{A}a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and in the case of what has been called a long shunt (fig. 2),

$$\mathrm{E}=\mathrm{Z}z-\mathrm{A}(a+s); \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in both cases, if C be the constant current supplied to the motor,

$$C = A + Z. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Fig. 1.

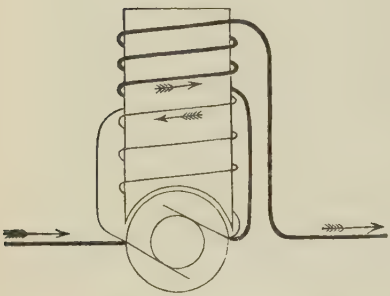
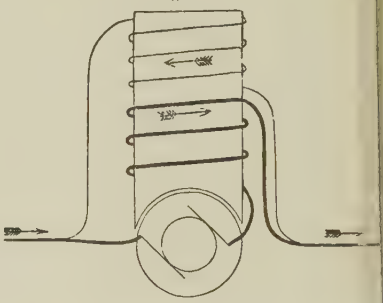


Fig. 2.



Now, remembering that in the case of a short shunt (fig. 1), C is equal to S, equations (1), (2), and (4) lead to

$$n\{p \pm q\,C \pm t\,(C-A)\} = (C-A)z - Aa; \quad . \quad . \quad (5)$$

and in the case of a long shunt (fig. 2), remembering that C is equal to A, equations (1), (3), and (4) lead to

$$n\{p \pm q\,A \pm t\,(C-A)\} = (C-A)z - A\,(a+s). \quad . \quad (6)$$

Equations 5 and 6 have then to be satisfied for all values of A for constant values of n and C; hence in the case of a short shunt,

$$\pm n\,(-tA) = -A\,(z+a), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and in the case of a long shunt

$$\pm n(q-t)A = -A\,(z+a+s). \quad . \quad . \quad . \quad . \quad (8)$$

But t, q, z, a, and s are all positive quantities, and since t is always larger than q, that is the number of turns in the shunt-coil is always larger than the number of turns in the series-coil, it follows that to satisfy either equation (7) for the short shunt or equation (8) for the long shunt, the positive value of t in the original equation (1) can in either case alone be employed. In other words, whatever be the arrangement of the series-coil, the shunt-coil must be a *magnetizing* and not a *demagnetizing* one.

This result we pointed out in our original paper on "Electromotors and their Government," in vol. xii. of the 'Journal of the Society of Telegraph Engineers and Elec-

tricians,' since on page 314 we stated that the solution for constant current was a shunt-motor with a series demagnetizing-coil; and it would be unnecessary to refer to this point again were it not that in one of the standard English treatises in which our method of governing motors is described in detail, the only solution for constant current that we are credited with is the *impossible* one of a series-motor with shunt demagnetizing-coil, the author not having observed that such a combination, whether used as a short or as a long shunt, could only make a motor run at a uniform speed when the speed was negative. Now, what does a negative value of n mean? It means that the armature must run the other way, or, in other words, that what was supposed to be a series-motor must in reality be the armature combined with a series demagnetizing-coil, that is must act as a series brake-dynamo, and the supposed shunt demagnetizing-coil must, in conjunction with the armature, act as a shunt-motor; or, in other words, the solution is as we originally stated it—a shunt-motor with series demagnetizing-coil.

In another important English work our method is given correctly, but it is stated that the method would not work, because when a greater load was put on the motor the armature would go more slowly, the back E.M.F. would therefore be diminished, and less current would pass round the shunt-coil of the field-magnet. Hence the field-magnet would be weakened, which would cause the motor to go more slowly, and so on until it stopped and possibly reversed. This objection is a curious one, because exactly the same apparent difficulty might have been stated by the author of this treatise when he was dealing with our method of governing motors to run at a constant P.D. a few pages earlier. Here, however, he sees the explanation of the difficulty, and he points out quite correctly that, although it might at first sight appear anomalous to say that, in order to keep a motor running at a fixed speed, it is necessary to weaken the field of the motor when the load on it is increased, the explanation is found in the fact that the power depends not merely on the strength of the field but on the current passing through the armature, and that this latter is much increased when the field is weakened. Hence, on the whole, it is quite right to arrange matters so

that the field is weakened when the load is increased. We say it is curious then, that while the author has explained the apparent difficulty so clearly when he was dealing with our method for governing motors when the supply condition was a constant P.D., he does not see that exactly the same explanation clears away the difficulty which he has himself raised regarding our method for governing motors to run when supplied with constant current.

What, however, we particularly wish to point out in this short note is that when the condition of supply is constant current it is not necessary to have a series demagnetizing-coil at all, and consequently the motor can be made to run at constant speed independently of the load, and in addition to work with high efficiency.

We will first see whether such a solution is possible when the condition of supply is constant P.D. Let the motor be a simple shunt-motor; then, if as before E be the back E.M.F., n the speed, p a term depending on the permanent magnetism, and Z the current round the shunt,

$$\mathrm{E} = n\,(p + t\,\mathrm{Z}); \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

also $$\mathrm{E} = \mathrm{Z}z - \mathrm{A}a,$$

if z be the resistance of the shunt-coil, A the current in the armature, and a the resistance of the armature; also

$$\mathrm{V} = \frac{\mathrm{Z}}{z},$$

where V is the constant P.D. maintained at the terminal, of the motor;

$$\therefore \quad n\left(p + t\frac{\mathrm{V}}{z}\right) = \mathrm{V} - \mathrm{A}a. \quad . \quad . \quad . \quad (10)$$

If n is to be constant as well as V, the left-hand side of the equation is constant, whereas the right-hand side varies with A the current through the armature, which must alter as the power given out by the motor alters. One solution for making this equation always true independent of the value of A is the well-known one of making a very small. When, however, a is not very small, and we have shown in detail elsewhere why we consider it a mistake to make the resistance of the armature as small in a motor as in a dynamo, equation (10) cannot be fulfilled for constant values of n and V, and

a variable value of A ; and in order that the equation may be made true a negative term proportional to A must be introduced on the left-hand side. The simplest way of doing this is to add a series demagnetizing-coil. Then (9) becomes

$$E = n\ (p - q\ A + tZ),$$

and (10)

$$n\left(p - q\ A + t\frac{V}{z}\right) = V - A\ (a + s),$$

an equation which will be always satisfied for any value of A if

$$n = \frac{a+s}{q}.$$

But when the supply is a constant current C supplied to the motor, the equation for a simple shunt-motor is

$$E = n\ (p + tZ),$$
$$E = Zz - Aa,$$
$$C = A + Z\ ;$$

and, therefore,

$$n\ \{p + t\,(C - A)\} = (C - A)z - Aa. \quad . \quad . \quad . \quad (11)$$

A now appears with a negative sign on both sides of the equation (11), and this equation will always be satisfied for any value of A if

$$n = \frac{z+a}{t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

without there being any necessity for using a series demagnetizing-coil. At first sight, then, it appears as if an entirely new solution for governing a motor supplied with a constant current had been arrived at, consisting simply of using a shunt-motor. But on further examination it is seen that if we substitute in (11) the value given in (12) for n, we obtain for C the current for which the motor governs :

$$C = \frac{np}{z - nt}$$
$$= -\frac{np}{a}.$$

But as this is negative it is necessary, in order that the shunt-motor may govern, that the terminals of the motor should be reversed. This will reverse the current round the field-magnet

but, by hypothesis, not the residual magnetism, otherwise p would also become negative. The core of the electromagnet must, therefore, be of steel, so strongly magnetized that the shunt-current does not reverse the polarity, and the permanent magnet and rotating armature together form a brake-dynamo while the shunt-coil and the armature will form the motor. But this is simply one of the solutions (a theoretical one of course and not a practical one) given by us on page 310 of our original paper and illustrated in figure 10 on that page.

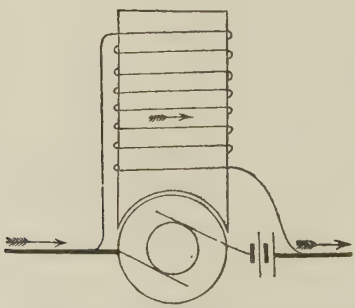
The fact, however, still remains that in the case of the supply condition being constant current, equation (11) can be satisfied without the employment of a series demagnetizing-coil; and all that we have to do to in order to make the solution a practical one, that is to enable an ordinary field-magnet with soft iron core to be employed, is to alter the equation so that when the speed equation (12) is satisfied (11) leads to a positive value of the current. This result may be obtained by adding to the right-hand side of equation (11) a positive constant term e numerically larger than np, for in that case, if

$$n = \frac{z+a}{t}$$

$$\mathrm{C} = \frac{e-np}{a}$$

for all values of A. Now such a positive term e will be

Fig. 3.



introduced on the right-hand side of equation e, if some accumulators of E.M.F. equal to e be introduced into the armature circuit, as in fig. 3, the accumulators being joined up so as to help the main current C. In that case the resistance

a of the armature must be increased by a', the resistance of the accumulators; and the two equations we are finally led to for the speed at which the motor governs, and the constant current for which it governs, are

$$n = \frac{z + a + a'}{t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$C = \frac{e - np}{a + a'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This solution is a practical one, and consists of a simple shunt-motor, with some accumulators in the armature circuit. Further, it is one not requiring many accumulators, for if np, the back E.M.F. of the motor due to the residual magnetism alone be small, as it will be if the field-magnet iron core be soft, and further, if $a + a'$ be also not large, e need not be large in order that the value of C, the current for which the motor governs, may be as large as we like. The essence of this new method for making a motor supplied with a constant current revolve at a constant speed independently of the load does not consist in combining a shunt-motor with a series brake-dynamo, which was the essence of our original method, but in combining a shunt-motor with a store of electric energy in the armature-circuit, which store of energy, as the equations show, is automatically dealt out to help the motor exactly in proportion as the demand for power is required to keep the speed constant when the load on the motor is varied. And this store can be easily maintained by reversing the connexions of the accumulators when they are disconnected from the motor, and the motor is at rest, and leaving the accumulators without supervision to be charged by the constant current that is continuously supplied to the station.

While on the subject of electromotors it may be well to point out a fact which we thought was well known, viz. that when motors are being tested one against another for efficiency and for power developed per pound weight, it is most important that the motors should each be supplied with the P.D. they are intended to work at and should be run at their normal speed. But we have been much astonished to find in the 'Technology Quarterly' for September last, published by the Massachusetts Institute of Technology, a

paper by Mr. H. Clifford on "The Efficiency of Small Electro-Motors," in which the results of experiments on the relative power and efficiency of a number of motors are given without any attention having been paid to the particular P.D. and speed at which each motor was wound to work at. Mr. Clifford's results are arranged in tables which would be of considerable practical value were it not that the essential condition for making such tests has been absolutely disregarded. Hence Mr. Clifford's tables are not only valueless but are most misleading. We are able to speak definitely on the subject, because the results of the tests made on a motor of ours, which are quoted, are made with the motor running at less than half its normal speed, and supplied with less than one quarter of its normal power. As well might incandescent lamps intended to be run with very different P.Ds. be compared when run with totally wrong P.Ds., and a 100-volt lamp condemned as useless because when supplied with only 50 volts it emitted but little light.

XLIII. *On the Formulæ of* Bernoulli *and of* Haecker *for the Lifting-power of Magnets. By* Professor Silvanus P. Thompson*.

Formulæ for the lifting-power of magnets have been given by D. Bernoulli and by Haecker, and more recently by Ván der Willigen.

Bernoulli's empirical rule† is that the lifting-power varies as the cube root of the square of the magnet's weight, or

$$P \propto \sqrt[3]{W^2},$$

where P is the lifting power or pull exerted by the magnet in contact with its keeper, and W the mass of the magnet.

Haecker‡ gave precision to the rule by introducing a coefficient, the numerical value of which varies with the qualities of steel employed. Writing

$$P = a\sqrt[3]{W^2},$$

he found that (when the unit of mass taken was the German

* Read May 26, 1888.

† *Acta Helvetica*, iii. p. 233 (1758).

‡ Pogg. *Ann.* lvii. p. 321 (1842).

pound) a had values between 8 and 10 for bar-magnets, and double these values for horseshoe-magnets. That is to say, according to Haecker a steel horseshoe-magnet weighing 1 pound could lift between 16 and 20 pounds, according to the quality of the steel and the intensity of its magnetization. The formula was found to be reasonably valid for magnets between $\frac{1}{120}$ pound up to 40 pounds in weight.

Van der Willigen *, repeating the investigation partly with Haecker's own magnets and partly with more recent magnets made by Von Wetteren, by Elias, and by Logeman, found a somewhat different empirical rule. According to him the permanent lifting-power should be written

$$P = bK\sqrt{A}\sqrt[4]{\frac{L}{\sqrt{A}}} \times \frac{L}{l};$$

where b is a constant depending on the quality of the steel and its degree of magnetization, K the perimeter of the polar surface, A the area of polar surface, L the length between the actual poles, and l the mean between interior and exterior lengths of the bar. For similar solids $K\sqrt{A}$ is simply proportional to the surface A; so that this formula if applied to similar magnets merely means that the lifting-power varies as the polar surface, multiplied by a correcting factor which takes into account the proximity of the two poles. Van der Willigen found the coefficient b, which is virtually the same as Haecker's a, to vary, for good horseshoe-magnets, from 19·5 to 22·5.

If we consider the meaning of Bernoulli's and Haecker's formulæ, as applied to magnets of similar form, we shall see that the cube root of the square of the mass of the magnet is a quantity simply proportional to its polar surface, for the linear dimensions are proportional to the cube root of the mass, and the surface to the square of the linear dimensions. Hence, so far as similar forms of magnet are concerned, these rules mean nothing more or less than that the lifting-power is proportional to the polar surface. This we know from Joule's and many subsequent researches to be approximately true for magnets carried to equal intensity of magnetization.

* *Sur le magnétisme des aimants artificiels*, par V. S. M. Van der Willigen (Haarlem, 1878).

Viewing the matter by the light of more recent researches on the induction of magnetism in closed circuits of iron or steel, we come to the same conclusion; for assuming that the magnetic induction B has been carried to an equal degree in the metal, the tension at any point in the circuit (in dynes per square centimetre) is*

$$T = \frac{B^2}{8\pi},$$

and the element of the pull over area dA is

$$dP = T dA = \frac{1}{8\pi} B^2 dA;$$

whence

$$P = \frac{1}{8\pi} \int B^2 dA,$$

which can be determined if the law of the distribution of the magnetic induction through the cross-section is known. Assuming this to be a simple uniform distribution (it is generally not quite so at the joint between the polar surfaces and armature of a magnet), this gives the pull (in dynes) as

$$P = \frac{1}{8\pi} B^2 A.$$

This formula† affords a very convenient method of reckoning B from measurements made upon the pull exerted at a given polar surface; the formulæ becoming

$$B = 5000 \sqrt{\frac{P \text{ kilos.}}{A \text{ sq. cm.}}};$$

or

$$B = 1317 \sqrt{\frac{P \text{ lbs.}}{A \text{ sq. in.}}}.$$

The a of Haecker's formula may, therefore, be taken as simply proportional to the square of the magnetic induction through the contact-surface, or

$$a = \frac{1}{8\pi} B^2 . d^{\frac{3}{2}} . c,$$

where d is the density of the steel, and c the ratio of the

* Maxwell's 'Electricity and Magnetism,' Art. 643.

† In Mr. Shelford Bidwell's paper, Proc. Roy. Soc. 1886, he uses a formula equivalent to $\frac{1}{8\pi}(B^2 - H^2)A$, but without giving any reason for deducting H^2 from B^2.

polar surface to the surface of one face of a cube of equal volume to that of the magnet.

Haecker found a for horseshoe-magnets twice as great as for bar-magnets. Van der Willigen found it from three to four times as great for horseshoes. Taking Haecker's figure, this shows that the long return-path through air of the tubes of magnetic induction offered so great a resistance that the steel magnet could only produce across the polar surface in this case an induction $\frac{1}{\sqrt{2}}$ times as great as when the closed horseshoe circuit was used.

Consideration of the rational formula will show that the greater lifting-power in proportion to their own weight possessed by small magnets, does not require for its explanation the sometimes alleged fact that small pieces of steel can be more highly magnetized than large pieces of steel. For, assuming equal intensity of magnetic induction, B, it is seen that the lifting-power is proportional to surface and not to weight; hence it must necessarily be greater relatively to weight in small magnets.

The net result of this paper is that Haecker's (and Bernoulli's) formula is merely another way of saying that the lifting-power of magnets in which the intensity of the magnetic induction has been carried up to an equal degree, is proportional to the polar surface. And Haecker's coefficient is proportional to B^2 through that surface.

XLIV. *The Function of Osmotic Pressure in the Analogy between Solutions and Gases.* *By* Professor J. VAN'T HOFF*.

DURING an investigation which required some knowledge of the laws regulating chemical equilibrium in solutions, the conclusion has gradually been evolved that a deep analogy —indeed almost an identity—exists between dilute solutions exerting osmotic pressure on the one hand, and gases under ordinary atmospheric pressure on the other. The following pages contain an attempt to explain this analogy; and the

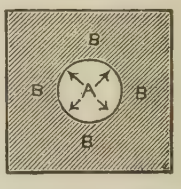
* Read June 9, 1888; translated by Prof. W. Ramsay, F.R.S.

physical properties of such systems will form the first subject of discussion.

I. *Osmotic Pressure—the nature of the Analogy due to this conception.*

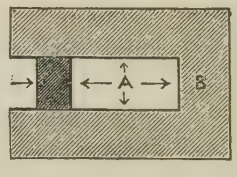
In order clearly to realize the quantity referred to as osmotic pressure, imagine a vessel, A (fig. 1), completely full of an aqueous solution of sugar, placed in water, B. If it be conceived that the solid walls of this vessel are permeable to water, but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby increasing the pressure on the walls of the vessel. Equilibrium then ensues, owing to the pressure resisting further entry of water. This pressure we have termed *osmotic pressure*.

Fig. 1.



It is evident that this state of equilibrium might have been attained in A without entry of water if the vessel had been constructed with a piston, compressing the solution with a pressure equal to the osmotic pressure (fig. 2). It follows moreover that, by increasing or diminishing the pressure on the piston, the state of concentration of the liquid can also be altered, owing to the passage of water through the walls of the vessel in an outward or inward direction.

Fig. 2.



Such osmotic pressure has been experimentally investigated by Pfeffer (*Osmotische Untersuchungen*, Leipsig, 1887). The walls of the cell consisted of unglazed porcelain, rendered impermeable to sugar though not to water, by filling it with a solution of potassium ferrocyanide and placing it in a solution of copper sulphate. Owing to diffusion, the ferrocyanide and the copper-salt come in contact after some time, and produce a membrane of copper ferrocyanide having the required properties. Such a vessel is then filled with a one-per-cent. solution of sugar; it is then closed with a cork provided with

a manometer, and sunk in water ; the osmotic pressure gradually rises, owing to entry of water, and the pressure due to the entry of water is read off when it becomes constant. As an example of the results obtained, it may be mentioned that a one-per-cent. solution of sugar (which, owing to its considerable mass, was not appreciably diluted on entry of water) exerted at 6°·8 a pressure of 50·5 millim. of mercury—about one fifteenth of an atmosphere.

The porous membrane, such as that described, will be termed in the following pages a "semipermeable membrane;" and the conception will be made use of even where experimental verification is lacking. The behaviour of solutions may thus be studied in a manner strikingly analogous to that employed in the study of gases, inasmuch as what is known as "osmotic pressure" corresponds to pressure, or, as it is commonly but incorrectly termed, "tension" of a gas. It is right to mention that this is no fanciful analogy, but a fundamental one ; the mechanism which, according to our present views, controls the pressure of gases and the osmotic pressure of liquids is substantially the same. In the former case pressure is due to the impacts of gaseous molecules on the walls of the containing vessel, and in the latter to the impacts of the molecules of the dissolved substance on the semipermeable membrane, since the impacts of the molecules of the solvent, being equal and opposed on each side of the vessel, may be neglected.

The great practical advantage arising from this method of regarding the behaviour of solutions, which leads at once to quantitative conclusions, consists in the fact that the application of the second law of thermodynamics to liquids is rendered exceedingly easy ; for reversible processes, of which this law treats, can now be very simply conceived. It has already been mentioned that a piston and cylinder with semipermeable walls, placed in the solvent, permits of alteration of concentration of the solution contained therein, by alteration of the pressure on the piston, in exactly the same way as a gas can be rarefied or compressed ; except that in the former case it is the solvent which escapes through the semipermeable walls on increase of pressure. Processes of this kind can always be made reversible, if care be taken that the pressure on the

piston is made equal to the opposed pressure, that is, in the case of solutions, the osmotic pressure.

We shall make use of this practical advantage in the following pages, particularly in investigating the laws of "ideal solutions;" that is to say, solutions so dilute as to be comparable with "ideal" or "perfect" gases, in which the action on one another of the dissolved molecules, as well as their actual volume compared with that of the space they inhabit, is so small as to be negligible.

II. Boyle's *Law for Dilute Solutions.*

The analogy between dilute solutions and gases acquires at once a quantitative form, if it be noted that in both cases alteration of concentration exercises a similar influence on pressure, and is in both cases proportional to the pressure.

This proportionality, which for gases goes by the name of Boyle's law, may be proved experimentally for liquids, as well as deduced theoretically.

Experimental Proof (*Determination of osmotic pressure for solutions of various concentrations*).—Let us first adduce Pfeffer's determinations (*Osmotische Untersuchungen*, p. 71) of the osmotic pressure (P) in sugar-solutions at the same temperature (13°·2 to 16°·1), and with varying concentrations (C):—

C.	P.	$\frac{P}{C}$
1 per cent.	535 millim.	535
2 „	1016 „	508
2·74 „	1518 „	554
4 „	2082 „	521
6 „	3075 „	513

The approximately constant quotients $\frac{P}{C}$ point conclusively to this proportionality between pressure and concentration.

Comparison of Osmotic Pressures by Physiological Methods.—Observations of de Vries ("Eine Methode zur Analyse der Turgorkraft," Pringsheim's *Jahrb.* xiv.) show that equal changes of concentration of solutions of sugar, and of potassium sulphate and nitrate, exercise equal influence on the osmotic pressure. This osmotic pressure was compared, by

physiological methods, with that of the contents of a plant-cell ; the protoplasmal envelope contracts when it is immersed in solutions possessing great attraction for water. By a systematic comparison of the three bodies mentioned, using the same cells, three *isotonic liquids* (*i. e.* liquids exhibiting the same osmotic pressure) were obtained. Cells of a different plant were then made use of, and so four *isotonic* series were constructed which showed a similar proportion in their concentrations ; this is exhibited in the following table, where the concentrations are expressed in gram-molecules per litre :—

Series.	KNO_3.	$C_{12}H_{22}O_{11}$.	K_2SO_4.	$KNO_3=1$.	$C_{12}H_{22}O_{11}$.	K_2SO_4.
I. .	0·12	—	0·09	1	—	0·75
II. .	0·13	0·2	0·1	1	1·54	0·77
III. .	0·195	0·3	0·15	1	1·54	0·77
IV. .	0·26	0·4	—	1	1·54	—

Theoretical Proof.—These observations render highly probable the existence of proportionality between osmotic pressure and concentration, and the theorem may be completed by a theoretical proof which is, indeed, almost self-evident. Regarding osmotic pressure as due to a kinetic cause (*i. e.* as produced by impacts of the dissolved molecules), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's law. If, on the other hand, osmotic pressure be regarded as the outcome of an attraction for water-molecules, its value is evidently proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and each one exerts its own special attractive action, uninfluenced by its neighbours.

III. Gay-Lussac's *Law for Dilute Solutions.*

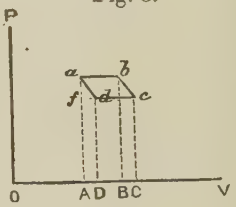
While the proportionality between concentration and osmotic pressure is self-evident, so long as temperature remains constant, the proportionality between osmotic pressure and absolute temperature, the concentration being maintained constant, is not so manifest. Yet proof can be furnished from thermodynamical considerations ; and experimental data exist

which are highly favourable to the results predicted on thermodynamical grounds.

Theoretical Proof.—It has been already mentioned that, by means of a piston and a cylinder with semipermeable walls, reversible processes can be conceived to occur. If such processes are expressed in the way common as regards gases, volume and pressures are indicated on the lines O V and O P (fig. 3); but pressure in this case, as before, must be taken as osmotic pressure. The initial volume (V cub. metres) is represented by OA; the initial pressure on the piston of area 1 square metre (P kilogr.) by A*a*; and the absolute temperature by T; the solution is then conceived to undergo a minute increase of volume, dV cubic metres (=AB), by moving the piston through dV metres, while the temperature of the solution is maintained constant by introduction of the requisite amount of heat. This amount of heat can be at once determined, inasmuch as it is equivalent to the external work performed, PdV, by the motion of the piston. Internal work is absent, for the dilution is, by hypothesis, so great that the dissolved molecules exercise no attraction on each other. This isothermal change *ab* is succeeded by the isentropic or adiabatic change *bc*, during which heat is neither absorbed nor evolved; the temperature sinks by dT°; and the original condition is then brought about by a second isothermal and a second adiabatic change, *cd* and *da*, respectively. The second law of thermodynamics requires that the fraction, $\frac{d\mathrm{T}}{\mathrm{T}}\mathrm{P}dV$ of the initially imparted heat charge PdV shall have been converted into work; this must be equivalent to the area *abcd*; and hence the equation follows: $\frac{d\mathrm{T}}{\mathrm{T}}\mathrm{P}dV = a\,b\,c\,d = af.\,\mathrm{AB} = af\,dV$; and hence $\mathrm{P}\frac{d\mathrm{T}}{\mathrm{T}} = af$. But *af* represents the change of osmotic pressure, volume being kept constant, due to the change of temperature dT; *i. e.* $\left(\frac{d\mathrm{P}}{d\mathrm{T}}\right)_{\mathrm{V}} d\mathrm{T}$; hence

$$\left(\frac{d\mathrm{P}}{d\mathrm{T}}\right)_{\mathrm{V}} = \frac{\mathrm{P}}{\mathrm{T}}.$$

Fig. 3.



On integration this equation gives, on the assumption of constant volume,

$$\frac{P}{T} = \text{constant};$$

that is, the osmotic pressure is proportional to the absolute temperature, provided concentration (which is here equivalent to the volume of a gas) remain constant; and this is entirely in accordance with Gay-Lussac's law connecting the pressure and temperature of gases.

Experimental Proof (*Determination of the osmotic pressure at different temperatures*).—Let us compare this theoretical conclusion with the experimental data furnished by Pfeffer (pp. 114–115). He found that the osmotic pressure increases with rise of temperature; it will be seen that, although his results do not furnish a conclusive proof of the correctness of the theorem, yet there is a most striking correspondence between experiment and theory. If we calculate from one of two experiments at different temperatures the osmotic pressure to be expected in the other, by help of Gay-Lussac's law, and compare it with the experimental result, we have the following series :—

1. Solution of cane-sugar.

Pressure at 32°, found . . .	544	millim.
Pressure at 14°·15, calculated .	512	„
„ „ found . .	510	„

2. Solution of cane-sugar.

Pressure at 36°, found . . .	567	„
Pressure at 15°·5, calculated .	529	„
„ „ found . .	520·5	„

3. Solution of sodium tartrate.

Pressure at 36°·6, found . .	1564	„
Pressure at 13°·3, calculated .	1443	„
„ „ found . .	1431·6	„

4. Solution of sodium tartrate.

Pressure at 37°·3, found . .	983	„
Pressure at 13°·3, calculated .	907	„
„ „ found . .	908	„

Comparison of the Osmotic Pressure by Physiological Methods.—In the same manner that support has been lent to the application of Boyle's law to solutions (viz. that different substances in *isotonic* solutions retain their equality of osmotic pressure so long as their respective concentrations are reduced to the same fraction), so the application of Gay-Lussac's law receives support by the fact that this isotonic state is maintained during equal alterations of temperature. It has been proved by physiological methods by Donders and Hamburger (*Onderzoekingen gedaan in het physiologisch. Laboratorium der Utrechtsche Hoogeschool* [3] ix. p. 26), making use of blood-corpuscles, that solutions of potassium nitrate, sodium chloride, and sugar, which at 0° are isotonic with the contents of these cells, and hence are isotonic with each other, exhibit the same isotonic state at 34°; this is seen in the annexed table :—

	Temperature 0°.	Temperature 34°.
KNO . . .	1·052 to 1·03 p. c.	1·052 to 1·03 p. c.
NaCl . . .	0·62 to 0·609 p. c.	0·62 to 0·609 p. c.
$C_{12}H_{22}O_{11}$ . .	5·48 to 5·38 p. c.	5·48 to 5·38 p. c.

Experimental Proof of Boyle's *and* Gay-Lussac's *Laws for Solutions. Experiments by* Soret (*Archives des Sciences phys. et nat.* [3] ii. p. 48 ; *Ann. Chim. Phys.* [5] xxii. p. 293).—The phenomenon observed by Soret lends a strong support to the analogy between dilute solutions and gases in respect of the influence of concentration and temperature on pressure. His work shows that just as in gases the warmest part is the most rarefied, so with solutions the warmest portions are the most dilute; but that in the latter case a much longer time must be allowed for the attainment of equilibrium. The experimental apparatus consisted of a vertical tube, the upper portion of which was heated while the lower portion was kept at a low temperature.

Soret's latest experiments lend a quantitative support to our analogy. As with gases, it is to be expected that when the isotonic state is produced, the solution will exist in equilibrium; and as the osmotic pressure is proportional to concentration and to absolute temperature, the isotonic state of different portions of the solution will occur when the

product of the two (absolute temperature and concentration) are equal. If we therefore calculate, on this basis, the concentration of the warmer part of the solution from data obtained with the colder, the values compare with those found as follows :—

1. *Solution of Copper Sulphate.*—The portion cooled to 20° contained 17·332 per cent. The hot portion at 80° should contain 14·3 per cent. ; found, 14·03 per cent.

2. The portion cooled to 20° contained 29·867 per cent. The portion at 80° should contain 24·8 per cent. ; found, 23·871 per cent.

It must be stated that previous experiments by Soret gave less favourable results ; yet perhaps too much importance should not be attached to them, owing to the difficulties of experiment.

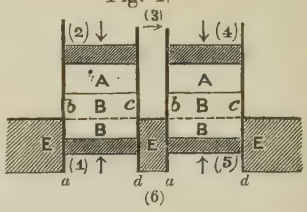
IV. Avogadro's *Law applied to Dilute Solutions.*

We have considered the changes produced in the osmotic pressure of solutions by alteration of temperature and concentration, and attempted to exhibit the analogy between dilute solutions and gases, in relation to these two quantities It now remains to compare directly the two analogous quantities, gaseous pressure and osmotic pressure, in one and the same body. It is obvious that this analogy should hold with gases in solution ; and in actual fact it will be shown that, if Henry's law be taken into consideration, the osmotic pressure in solution is absolutely equal to the gaseous pressure, under similar conditions of temperature and concentration.

To prove this statement, we shall picture a reversible process by aid of semipermeable diaphragms, temperature being maintained constant ; and we shall again make use of the second law of thermodynamics, which in this case leads to the simple result that no work is transformed into heat, nor heat into work ; and hence the sum of all work done at different stages of the process is zero.

This reversible process may be conceived by means of two similar cylinders and pistons, like those already described. One contains a gas (A), say oxygen, and in contact with it a saturated aqueous solution of oxygen (B) (fig. 4). The wall *b c*

Fig. 4.



allows only oxygen to pass, but no water; the wall ab, on the other hand, water, but not oxygen; and it is in contact with water, E. A reversible process may be carried out by such an arrangement as follows:—By raising the two pistons (1) and (2), oxygen is evolved from its aqueous solution as gas, while the water passes through ab; this change can proceed without altering the concentration of the solution. The only difference between the two cylinders is in the state of concentration of the solutions which they contain; we may explain the action thus:—The unit of weight of the substance in question occupies in the left-hand cylinder a volume v and V, and in the right-hand cylinder, $v+dv$ and $\mathrm{V}+d\mathrm{V}$; hence, in order that Henry's law may hold,

$$v : \mathrm{V} = (v+dv) : (\mathrm{V}+d\mathrm{V}); \text{ hence } v : \mathrm{V} = dv : d\mathrm{V}.$$

If, now, the pressure, or osmotic pressure, as the case may be (supposing unit volume to contain unit mass), as regards gas and solution be P and p (which will afterwards be shown to be equal), then, from Boyle's law, the pressure in gas and solution will be $\frac{\mathrm{P}}{v}$ and $\frac{p}{\mathrm{V}}$ respectively.

Now let the pistons (1) and (2) be raised so as to liberate unit weight of gas from the solution, and increase the gaseous volume v by dv, in order to equalize its concentration with that of the gas in the left-hand vessel, and by depressing the pistons (4) and (5) let us redissolve the freshly liberated gas, and then reduce the volume of the solution $\mathrm{V}+d\mathrm{V}$ by the amount $d\mathrm{V}$ in the cylinder with semipermeable walls; then the cycle is complete.

Work has been done in six separate ways; let us number them (1), (2), (3), (4), (5), and (6). Now (2) and (4) are equal in amount, but opposite in sign, since they refer to change of volume v and $v+dv$ in opposite directions under pressures which are inversely proportional to the volumes. In similar manner the sum of (1) and (5) is zero; so that the point requiring proof is that $(3)+(6)=0$. Here (3) repre-

sents work done by the gas in increasing its volume by dv, under a pressure of $\frac{P}{v}$, therefore $(3)=\frac{P}{v}dv$; while (6) represents the work done by the solution, while it decreases in volume by $d\mathrm{V}$, under a pressure of $\frac{p}{\mathrm{V}}$, therefore $(6)=-\frac{p}{\mathrm{V}}d\mathrm{V}$. The statement is therefore

$$\frac{P}{v}dv=\frac{p}{V}d\mathrm{V};$$

and as $v:\mathrm{V}=dv:d\mathrm{V}$, P must be equal to p, which was to be proved.

This conclusion, which will receive in the sequel ample confirmation, lends, on the one hand, support to Gay-Lussac's law in its application to liquids:—If gaseous pressure and osmotic pressure are at the same temperature equal to one another, then equal changes of temperature must affect both equally. On the other hand, this relation allows of a considerable extension of Avogadro's law, always provided that we may substitute the conception of osmotic pressure for gaseous pressure:—under equal osmotic pressures and at the same temperature, equal volumes of all solutions contain equal numbers of molecules; and, moreover, the same number of molecules which would be contained in an equal volume of a gas under the same conditions of temperature and pressure.

V. *General Expression for* Boyle's, Gay-Lussac's, *and* Avogadro's *Laws for Solutions and Gases.*

The well-known formula expressing both Boyle's and Gay-Lussac's laws for gases,

$$PV=RT,$$

are, in so far as these laws are applicable to liquids, also applicable as regards osmotic pressure; with the reservation, also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the molecules becomes negligible.

To include Avogadro's law in the above expression, Horstmann's suggestion (*Berl. Ber.* xiv. p. 1243) may be adopted, to express the molecular weight of the substance in kilograms;

taking 2 kilos. of hydrogen, 44 kilos. of carbon dioxide, and so on. Then R in the above equation has always the same value; for, under equal conditions of temperature and pressure, these weights occupy the same volume. Calculating this value, and expressing the volume in cubic metres, and the pressure in kilograms per square metre, and choosing hydrogen gas at 0° and 760 millim. pressure as starting-point, then

$$P=10333;\quad V=\frac{2}{0{\cdot}08956};\quad T=273;\quad R=845{\cdot}05.$$

Hence the combined expression for Boyle's, Gay-Lussac's, and Avogadro's laws becomes

$$PV=845T;$$

and this expression is applicable to solutions, substituting osmotic pressure for gaseous pressure.

We may give this equation even a simpler form, inasmuch as the number of calories equivalent to a kilogrammetre of work ($A=\frac{1}{J}=\frac{1}{423}$) stands in a very simple relation to R, viz. $AR=2$ (in reality about one thousandth less). Hence we may choose the form

$$APV=2T;$$

and this form has the great practical advantage that work, which will often be discussed in the following pages, receives a very simple expression, if calculated back to heat, measured in calories.

Let us next calculate the work, expressed in calories, when a gas or a solution, under constant pressure and temperature, expands V volumes; V volumes containing a kilogram-molecule. This is evidently 2T. It must be added that this constant pressure is maintained only when the total volume of gas or solution is very great compared with V, or in cases of evaporation, where the vapour-pressure is at its maximum.

We shall also often have to express in calories the work done during isothermal expansion of the kilogram-molecule of a substance as gas, or in solution. If pressure falls a very small fraction ΔP, corresponding to a small increase of volume ΔV, the work done will be $AP\Delta V$, or $2\Delta T$.

VI. *First Confirmation of* Avogadro's *Law in its Application to Solutions.—Direct determination of Osmotic Pressure.*

It is to be expected that Avogadro's law, deduced as a consequence of Henry's law for solutions of gases, will not be restricted to solutions of substances which usually exist in a gaseous condition. This expectation has been realized, not merely from a theoretical, but from an experimental standpoint. Pfeffer's determinations of the osmotic pressure of solutions of sugar furnish a remarkable confirmation of this extension of the law.

Pfeffer's solution consisted of 1 gram of sugar dissolved in 100 grams of water; one gram of the sugar therefore exists in about 100·6 cubic centim. of the solution. Comparing the osmotic pressure of this solution with the pressure of a gas (*e. g.* hydrogen) containing as many molecules in the volume, there are $\frac{2}{342}$ gram ($C_{12}H_{22}O_{11}=342$) in 100·6 cubic centim. Now one litre of hydrogen gas at 0° and 760 millim. pressure weighs 0·08956 gram; and the above concentration is equivalent to 0·0581 gram per litre; the pressure at 0° is 0·649 atmosphere, and at t, $0{\cdot}649(1+0{\cdot}00367t)$. Placing these results beside Pfeffer's, we obtain the following agreement:—

Temperature (t).	Osmotic pressure.	$0{\cdot}649(1+0{\cdot}00367t)$.
6·8	0·664	0·665
13·7	0·691	0·681
14·2	0·671	0·682
15·5	0·684	0·686
22·0	0·721	0·701
32·0	0·716	0·725
36·0	0·746	0·735

The directly determined osmotic pressure of a solution of sugar is thus seen to be equal to the pressure of a gas at the same temperature, containing the same number of molecules in unit volume as the sugar-solution.

Starting from cane-sugar, this relation can be calculated for other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate and citrate, all of which, from de Vries' physiological researches (*Eine Methode zur Messung der Turgorkraft*, p. 512), exhibit equal osmotic pressure when they contain an equal number of molecules in a given volume.

VII. *Second Confirmation of* Avogadro's *Law in its Application to Solutions.—Molecular lowering of Vapour-pressure.*

The relation between osmotic pressure and the pressure of a vapour in contact with liquid, which is easily developed on thermodynamical principles, yields, from Raoult's recent observations, a satisfactory proof of the analogy under consideration.

We shall begin with a general law, of which the previous matter of this thesis is quite independent:—*Isotonism* (*i. e.* equal osmotic pressure—from ἴσος and τόνος, *stretching*) *in solutions made with the same solvent, implies equality of vapour-pressure.* This statement is easily proved by a reversible cycle, keeping temperature constant. Imagine two solutions exhibiting equal vapour-pressure, and introduce a small quantity of one in the state of vapour into the other in a reversible manner, *i. e.* by means of cylinder and piston. The vapour-pressures are equal, hence this transference takes place without expenditure of work ; and also, on restoring the original condition, no work is expended. But if the solvent be transferred back through a semipermeable diaphragm, separating the two solutions, then equal osmotic pressure must exist, else the transference could not take place without expenditure of energy.

If this fundamental conception be applied to dilute solutions, accepting the laws which have been explained in the preceding pages, the simple conclusion follows, that if a solvent contains equal numbers of molecules of dissolved substances, the vapour-pressure is the same. This is merely Raoult's law (*Comptes rendus*, lxxxvii. p. 167 ; xliv. p. 1431) of the constancy of molecular diminution of vapour-pressure, obtained by multiplying the relative diminution by the molecular weight of a one-per-cent. solution ; *i. e.* with the difference between the vapour-pressures of the solvent, before and after addition of dissolved substance. The equality of molecular diminution of vapour-pressure depends on the solutions containing equal numbers of molecules, a close proportionality between the lowering of the vapour-pressure and the concentration being assumed. With ether, for example, the value fluctuated between 0·67 and 0·74 (mean 0·71) for thirteen substances dissolved in it.

But this relation can be further developed. Different

solutions may be compared with each other, and a second law may be deduced, which Raoult has also discovered experimentally. The following reversible process, consisting of two operations, is carried out with a very dilute solution of P per cent., at temperature T.

1. Remove, by use of cylinder with semipermeable wall, a portion of the solvent containing a kilogram-molecule (M) of the dissolved substance : here the total quantity of solution is supposed so great that no alteration of concentration occurs, and the expenditure of work is therefore 2T.

2. This quantity, $\frac{100\,M}{P}$ kilograms, of the solvent is returned as vapour ; it may be conceived as produced from the liquid by evaporation at its vapour-pressure ; then expanded till its pressure is equal to the vapour-pressure of the solution ; and finally liquefied in contact with the solution. The kilogram-molecule of the solvent (M′) will thus receive an expenditure of work of $2T\Delta$, where Δ represents the relative diminution of pressure ; and the $\frac{100\,M}{P}$ kilograms will receive $2T\Delta\frac{100\,M}{PM'}$. Here $\frac{\Delta}{P}M$ is Raoult's molecular diminution of pressure, which we shall term K ; employing this abbreviation, the expression becomes $\frac{200\,TK}{M'}$.

From the second law of thermodynamics, again, the algebraic sum of the work expended during this cycle at constant pressure must equal zero ; hence the work done by the solution during the first stage must equal the work done on it during the second ; and thus

$$2T = \frac{200\,TK}{M'}\text{ ; or }100\,K = M'.$$

This expression includes all Raoult's results. It expresses the fact, as stated above, that the molecular diminution of vapour-pressure is independent of the nature of the dissolved body ; and it also expresses, what Raoult found experimentally, that this diminution is independent of temperature. It also contains Raoult's second conclusion, that the molecular diminution is proportional to the molecular weight of the solvent, amounting to about one hundredth of the latter. This is seen from the following table :—

Solvent.	Molecular weight. (M').	Molecular diminution of vapour-pressure. (K).
Water	18	0·185
Phosphorous chloride . .	137·5	1·49
Carbon disulphide . . .	76	0·80
Carbon tetrachloride . .	154	1·62
Chloroform	119·5	1·30
Amylene	70	0·74
Benzene	78	0·83
Methyl iodide	142	1·49
Methyl bromide . . .	109	1·18
Ether	74	0·71
Acetone	58	0·59
Methyl alcohol	32	0·33

VIII. *Third Confirmation of* Avogadro's *Law in its Application to Solutions.—Molecular Depression of Freezing-point of Solvent.*

Here, again, a general law may be stated, connecting osmotic pressure with the freezing-point of a solution:—*Solutions in the same solvent, and of the same freezing-point, are isotonic at that temperature.* This statement admits, like the former, of proof by means of a reversible cycle ; but the solvent when returned is here in the condition of ice, not of vapour ; the inverse change is also brought about by means of a semipermeable diaphragm, and, as it cannot be accompanied by gain or loss of energy, isotonism must exist.

We shall apply the above statement to dilute solutions; and applying the relations previously described, the simple conclusion follows that solutions containing an equal number of molecules in equal volume, and which therefore, from Avogadro's law, are isotonic, also have the same freezing-point. This law has been actually discovered by Raoult, and is expressed by him as "normal molecular depression of freezing-point." It holds for the great majority of dissolved substances examined, and consists in the statement that the depression of freezing-point of a one-per-cent. solution, multiplied by the molecular weight of the dissolved substance, gives a constant

product; it is stated of solutions containing equal numbers of molecules in unit volume, assuming a close proportionality between concentration and lowering of the freezing-point. For an aqueous solution of nearly all organic bodies the constant product is about 18·5.

We can follow this relation still further, and, assuming Avogadro's law for solutions, deduce the above normal molecular depression of the freezing-point from other data. It bears a close relation to the heat of fusion of the solvent, as is shown by applying the second law of thermodynamics to a reversible cycle. Imagine a very dilute solution containing P per cent. of a dissolved substance, which has produced a depression of freezing-point, Δ; the solution itself freezes at T, and its heat of fusion is W per kilogram.

1. By use of piston and cylinder with semipermeable walls, the solution is deprived at temperature T of that amount of the solvent in which a kilogram-molecule of the dissolved substance existed; the amount of the solution is moreover so great that no appreciable change of concentration occurs, hence the work expended on it is 2T.

2. This quantity of solvent, $\frac{100\,M}{P}$, is then allowed to freeze at T by withdrawing $\frac{100\,MW}{P}$ calories; the solution and the solvent, now solid, are cooled through Δ degrees, and the solvent is now allowed to melt in contact with the solution, thereby absorbing the above quantity of heat. Finally, the temperature is raised Δ degrees.

During this reversible process $\frac{100\,MW}{P}$ calories rise from Δ to T, corresponding to an expenditure of energy equal to $\frac{100\,MW\Delta}{PT}$. In this expression, however, $\frac{M\Delta}{P}$ is the molecular depression of the freezing-point, which we may represent by the letter t; the work done is therefore $\frac{100\,Wt}{T}$, and it was shown above to be equal to 2T. Hence the equation

$$\frac{100\,Wt}{T} = 2T\,;\ \text{whence}\ t = 0{\cdot}02\,\frac{T^2}{W}.$$

This theoretical deduction receives ample confirmation from

experimental data. The following table exhibits the molecular depression of freezing-point experimentally determined by Raoult (*Annales de Chimie et de Physique*, [5] xxviii.; [6] xi.), along with the values calculated by means of the above formula :—

Solvent.	Freezing-point (T).	Heat of fusion (W).	$t=\frac{0{\cdot}02\,T^2}{W}$.	Raoult's molecular depression.
Water . . .	273	79	18·9	18·5
Acetic acid .	273+16·7	43·2*†	38·8	38·6
Formic acid .	273+ 8·5	55·6*†	28·4	27·7
Benzene . .	273+ 4·9	29·1†	53	50
Nitrobenzene .	273+ 5·3	22·3†	69·5	70·7

It may be added that, from the molecular depression of ethylene bromide (117·9), the hitherto unknown heat of fusion is found equal to 13 ; and Mr. Pettersson, at my request, having experimentally determined this constant, obtained the number 12·94.

IX. *Application of* Avogadro's *Law to Solutions.—The Law of* Guldberg *and* Waage.

Having discussed the physical aspect of this problem in order to furnish as many proofs as possible of the correctness of its treatment, it now remains to apply it to chemical facts.

The most evident application of Avogadro's law in reference to solutions is to the determination of the molecular weights of dissolved substances. This has already been attempted ; but here it is not the pressure which requires measurement, as with gases, when the molecular weight is deducible from volume, pressure, and temperature ; with solutions the osmotic pressure must be measured, and as yet the practical method is wanting. Yet this difficulty may be avoided by substituting for a determination of pressure that of the related values ; as, for example, the diminution of vapour-pressure, or the depression of the freezing-point. This proposal is Raoult's. He divides the reduction of vapour-pressure of water containing one per cent. of dissolved substance into 0·185 parts, or the observed depression of freezing-point into 18·5 parts ; and

* Berthelot, *Essai de Mécanique Chimique.*

† Pettersson, *Journ. f. prakt. Chem.* [2] xxvi. p. 129.

this method is comparable in respect of accuracy with determinations of the density of gases, and is in itself a strong presumption of the accuracy of Avogadro's law in its application to gases.

It is still more remarkable that the law of Guldberg and Waage, so generally accepted for solutions, can be evolved from the above laws regulating the behaviour of dilute solutions. Again, a reversible cycle at constant temperature must be imagined, which can be conceived for solutions equally well with gases, by means of semipermeable diaphragms.

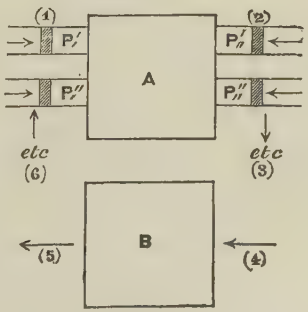
Let there be two systems of gaseous or dissolved substances in equilibrium, which may be expressed by the following symbols :—

$$a_{,}'\,M_{,}' + a_{,}''\,M_{,}'' + \&c. \rightleftarrows a_{,,}'\,M_{,,}' + a_{,,}''\,M_{,,}'' + \&c.,$$

where a denotes the number of molecules, and M the formula. This equilibrium exists in two different vessels, A and B, at the same temperature but at different concentrations, shown by the partial pressure, or by the osmotic pressure which each of the bodies exerts. Let these pressures be in vessel A, $P_{,}'\,P_{,}'' \ldots P_{,,}'\,P_{,,}''$ &c.; and in B greater than these by $dP_{,}'$ $dP_{,}'' \ldots dP_{,,}'\,dP_{,,}'' \ldots$ &c.

The reversible cycle consists in introducing into A that amount in kilograms expressed by the first symbol of the first system, while the second is removed in equivalent amount: both systems have here the concentrations which exist in A (fig. 5). This change is accomplished by causing the entry or exit of each of the substances in question by means of its own cylinder and piston, which is separated from A by a diaphragm permeable to that body alone. If they are in solution, then the cylinders possess a semipermeable wall, and are surrounded by the solvent.

Fig. 5.



When this has been done, each constituent of the two systems has undergone such a change of concentration that it is now equal

to that in B; and, as before, the work done per kilogram-molecule equals $2\Delta T$, where Δ represents a minute fraction of the pressure, and is here $\frac{dP}{P}$; for the amounts here in question it is $2aT\frac{dP}{P}$.

By making use of the vessel B, the second system, which has just been evolved, is now converted into the first, but of concentration as in B, proceeding as just described; and by suitable alteration of volume it is finally changed into its original state, as it at first existed in A.

As no change of temperature has occurred, the algebraic sum of all these operations is zero, as is seen from the numbers; it is thought unnecessary to interpret them, as they refer to the operations in the order in which they were carried out:— $(1)+(2)+(3)+(4)+(5)+(6)=0$.

Now (1) and (5) refer to operations opposite in sign on the same substances, with the same mass, at the same temperature; hence $(1)+(5)=0$. And for similar reasons, $(2)+(4)=0$; whence $(3)+(6)=0$.

This conclusion leads directly to Guldberg's and Waage's law.

The work expressed by (3) is from that law $\Sigma 2a_{,,}T\frac{dP_{,,}}{P_{,,}}$, and (6) is $\Sigma 2a_{,}T\frac{dP_{,}}{P_{,}}$; hence it follows that

$$\Sigma\left(2a_{,,}T\frac{dP_{,,}}{P_{,,}}-2a_{,}T\frac{dP_{,}}{P_{,}}\right)=0, \text{ or } \Sigma\left(a_{,,}\frac{dP_{,,}}{P_{,,}}-a_{,}\frac{dP_{,}}{P_{,}}\right)=0.$$

By integrating,

$$\Sigma(a_{,,}\log P_{,,}-a_{,}\log P_{,})=\text{constant};$$

and here P is proportional to the concentration, or to the active mass C; so that C may be substituted without altering the equation:—

$$\Sigma(a_{,,}\log C_{,,}-a_{,}\log C_{,})=\text{constant}.$$

This is the logarithmic form of Guldberg's and Waage's formula.

X. *Deviation from* Avogadro's *Law in Solutions.—Variations in* Guldberg *and* Waage's *Law.*

We have attempted to show the connexion between Guld-

berg and Waage's law and the laws of Boyle, Henry, Gay-Lussac, and Avogadro, as applied to liquids; as applied to gases, the truth of Guldberg and Waage's law has been long proved from thermodynamical considerations.

It remains to develop further the laws of chemical equilibrium, and, first, to investigate more closely the limits of applicability of the three fundamental principles from which Guldberg and Waage's law has been deduced.

So long as "ideal solutions" are under consideration, there exists strict analogy between gases and solutions; and just as there are deviations from Avogadro's law in the case of gases, so we may expect to find them with solutions. As, for example, the pressure of the vapour of ammonium chloride was found to be too great to be accounted for by Avogadro's law, so the osmotic pressure is in many cases abnormal; and as the high pressure in the first case is due to dissociation into ammonia and hydrogen chloride, it may be conceived that similar dissociation occurs in solutions. It must, indeed, be acknowledged that deviations are much more frequent with solutions than with gases, and occur often with bodies the dissociation of which, under ordinary circumstances, does not appear probable; in aqueous solution, for example, the majority of salts as well as the stronger acids and bases undergo dissociation; and hence Raoult did not discover the existence of so-called normal molecular depression of freezing-point and lowering of vapour-pressure until he investigated organic compounds; their behaviour is almost without exception regular. For these reasons it may have appeared daring to begin by giving prominence to Avogadro's law in its application to solutions; and I should have shrunk from this course had not Arrhenius pointed out to me the probability that salts, and analogous bodies, decompose on solution into their ions; in fact, substances which obey Avogadro's law are, as a rule, non-conductors, suggesting that in such cases no dissociation into ions occurs; and further experimental proof exists for other liquids, since by Arrhenius's assumption the deviations from Avogadro's law are calculable from the conductivity.

However this may stand, an attempt is made in the following pages to take account of such deviations from Avogadro's law, and, by help of the application of Boyle's and Gay-

Lussac's laws to solutions, to develop Guldberg's and Waage's formula so far as is possible.

The change in the expressions given above caused by these deviations is easily sketched.

The general expression for Boyle's, Gay-Lussac's, and Avogadro's laws, shown on p. 317, is

$$APV = 2T;$$

and this changes, if pressure is i-times that of this equation, into

$$APV = 2iT.$$

Hence, in a reversible cycle, the work will be i-times that previously done; this alteration is easily applied to the former statement of Guldberg's and Waage's formula. Recurring to the final stage of the cycle described on p. 325,

$$(3)+(6)=0,$$

the work corresponding to (3) and (6), which were formerly $\Sigma 2a_{,,}T\frac{dP_{,,}}{P_{,,}}$, and $-\Sigma 2a_{,}T\frac{dP_{,}}{P_{,}}$, is now increased i-times; hence the equations become

$$\Sigma\left(a_{,,}i_{,,}\frac{dP_{,,}}{P_{,,}}-a_{,}i_{,}\frac{dP_{,}}{P_{,}}\right)=0;$$

and on integration,

$$\Sigma(a_{,,}i_{,,}\log P_{,,}-a_{,}i_{,}\log P_{,})=\text{constant}.$$

And introducing the concentration, or the active mass C, instead of the pressure proportional to it,

$$\Sigma(a_{,,}i_{,,}\log C_{,,}-a_{,}i_{,}\log C_{,})=\text{constant}.$$

This is Guldberg's and Waage's law in a logarithmic form, differing from the former statement only by the introduction of the value i.

It remains to be shown that in this new form it agrees better with experimental results; and as a knowledge of the correct value of i is necessary, we must deal with aqueous solutions, for sufficient experimental data are to be had only with such.

XI. *Determination of* i *for Aqueous Solutions.*

— As Avogadro's law has been proved for solutions by four separate lines of argument, there are four ways in which the

deviations, *i. e.* the values of i, may be determined. But that one which depends on the lowering of the melting-point has been so thoroughly proved experimentally that we shall confine ourselves to its use.

Reverting to the cycle which, on p. 323, was employed to prove the applicability of Avogadro's law to solutions, the relation was found :—

$$\frac{100\,Wt}{T}=2T,$$

where the second term refers to the work done in removing or adding that amount of the solvent in which a kilogram-molecule of the substance was dissolved ; that term must therefore be multiplied by i :—

$$\frac{100\,Wt}{T}=2iT.$$

In this manner a simple means of determining the value of i is apparent. The value of i is from the above equation proportional to t, *i. e.* to the molecular depression of temperature, for the other data (T = absolute melting-point, W = heat of fusion of solvent) are constant. Now 18·5 is the molecular depression for cane-sugar, which from p. 319 is seen to follow Avogadro's law accurately ; hence $i=1$; and for other bodies i is their respective depressions divided by 18·5. Almost identical results are arrived at by using in the above equation, instead of T and W, the values for ice, viz. 273 and 79 ; they will therefore be employed in the following calculations.

XII. *Proof of the Modified Law of* Guldberg *and* Waage.

In employing the relation proposed for the purpose of comparison with the results of Guldberg and Waage's formula, it is necessary to mention the different forms which it has assumed during the years since its discovery. We shall first give this relation a simple expression in which Guldberg and Waage's conceptions may be included, viz. :—

$$\Sigma ai \log C=K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This differs from the one given on p. 328 merely in that the terms representing the components of both systems have had their signs changed. The original expression of the Nor-

wegian investigators is closely analogous (*Christiania Videnskabs Selskabs Forhandlingar*, 1864) :—

$$\Sigma k \log C = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

except that k has to be determined for each constituent in question by observation of the equilibrium of the system.

As Guldberg and Waage (*Études sur les affinités chimiques*, 1867) repeatedly found the coefficient k equal to 1, they simplified their equation thus :—

$$\Sigma \log C = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In their last treatise, however (*Jour. für prakt. Chem.* xix. p. 69), they introduce the change that the number of molecules a must also be taken account of, and consequently they approximate their formula to that deduced for gases on thermodynamical grounds, thus :—

$$\Sigma a \log C = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We have taken this last expression as their final formula.

The Norwegian investigators maintained this simple formula, with whole numbers as coefficients, even for solutions ; but Lemoine has lately revived the original formula (2) in order to represent the results of Schlösing's investigations on the solubility of calcium carbonate in water containing carbon dioxide, with constants hereafter to be determined, which are, however, not whole numbers ; for if whole numbers be employed, it is impossible to reconcile fact with theory.

In view of this uncertainty, the formula which we have suggested has this advantage, that the coefficients which occur in it are *a priori* determined, and its truth can at once be decided by experiment. It will in fact appear that in the instances studied by Guldberg and Waage the simple form which they recommend is completely confirmed ; and that such simplification is in most cases admissible confirms, moreover, the validity of Avogadro's law in its application to solutions. On the other hand, the results of Schlösing's investigation, prominently alluded to by Lemoine, cannot be simply expressed, and require the same fractional coefficients which Schlösing himself arrived at.

Before proceeding to this investigation, it is necessary to include cases where partially insoluble bodies are present:

this is easily done; they may be included in the formulæ given above, remembering that such bodies exist in solution up to its saturation-point, and are therefore present with constant concentration. All concentrations depending on this may, therefore, be removed from the first term of the above equation to the second, without affecting the constancy of the latter. Everything remains the same, except that in the first term only the dissolved bodies need be considered.

1. We shall first examine Guldberg and Waage's observations. The first case they studied was that expressed by the equation

$$BaCO_3 + K_2SO_4 \rightleftarrows BaSO_4 + K_2CO_3;$$

and they found, according to their simplified formula, that

$$\log C_{K_2SO_4} - \log C_{K_2CO_3} = K.$$

The relation given by our equation is almost identical, for, for K_2SO_4, $a=1$ and $i=2{\cdot}11$, and for K_2CO_3, $a=1$ and $i=2{\cdot}26$; hence

$$\log C_{K_2SO_4} - 1{\cdot}07 \log C_{K_2CO_3} = K.$$

A similar agreement exists with sodium carbonate, for then the values of i for Na_2SO_4 and Na_2CO_3 are 1·91 and 2·18 respectively; hence

$$\log C_{Na_2SO_4} - 1{\cdot}14 \log C_{Na_2CO_3} = K.$$

2. This result, expressed in what is almost a whole number, cannot be expected in the above-mentioned experiment of Schlösing (*Comptes rendus*, lxxiv. 1552; lxxv. 70). There the subject of experiment was the solubility of calcium carbonate in water containing carbonic acid, and the state of equilibrium is expressible by the following statement:—

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$

We should expect that, as $i=1$ for carbon dioxide, that i should $=2{\cdot}56$ for calcium hydrogen carbonate:—

$$0{\cdot}39 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K;$$

and Schlösing found:—

$$0{\cdot}37866 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K.$$

Similar experiments with barium are equally satisfactory;

the value of i for barium hydrogen carbonate is 2·66, and the following results are calculated :—

$$0{\cdot}376 \log C_{H_2CO_3} - \log C_{B\,(HCO_3)_2} = K.$$

The experimental result is

$$0{\cdot}38045 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K.$$

3. Turning to Thomsen's investigation on the action of sulphuric acid on sodium nitrate in solution (Thomsen's *Thermochemische Untersuchungen*, i.), we find a similar agreement.

The reaction may be formulated thus :—

$$Na_2SO_4 + HNO_3 \rightleftarrows NaHSO_4 + NaNO_3;$$

and Guldberg and Waage's relation requires

$$\log C_{Na_2SO_4} + \log C_{HNO_3} - \log C_{NaHSO_4} - \log C_{NaNO_3} = K.$$

Now

$i_{Na_2SO_4} = 1{\cdot}91$; $i_{HNO_3} = 1{\cdot}94$; $i_{NaHSO_4} = 1{\cdot}88$; and $i_{NaNO_3} = 1{\cdot}82$; and the equation becomes

$$1{\cdot}05 \log C_{Na_2SO_4} + 1{\cdot}06 \log C_{HNO_3} - 1{\cdot}03 \log C_{NaHSO_4} - \log C_{NaNO_3} = K,$$

which is almost identical.

If we express the relation thus :—

$$Na_2SO_4 + 2HNO_3 \rightleftarrows H_2SO_4 + 2NaNO_3,$$

Guldberg and Waage's formula becomes

$$\log C_{Na_2SO_4} + 2 \log C_{HNO_3} - \log C_{H_2SO_4} - 2 \log C_{NaNO_3} = K;$$

and we obtain :

$$\log C_{Na_2SO_4} + 2{\cdot}03 \log C_{HNO_3} - 1{\cdot}07 \log C_{H_2SO_4} - 1{\cdot}91 \log C_{NaNO_3} = K.$$

Again an almost absolute agreement.

4. Ostwald's investigation (*J. prakt. Chem.* [2] xix. p. 480) on the action of hydrochloric acid on zinc sulphide, according to the formula

$$ZnS + 2HCl \rightleftarrows H_2S + ZnCl_2,$$

leads, when the following values are ascribed :

$$i_{HCl} = 1{\cdot}98\ ;\ i_{H_2S} = 1{\cdot}04\ ;\ i_{ZnCl_2} = 2{\cdot}53$$

to the equation :—

$$3{\cdot}96 \log C_{HCl} - 1{\cdot}04 \log C_{H_2S} - 2{\cdot}53 \log C_{ZnCl_2} = K.$$

It is evident that the concentrations of the sulphuretted hydrogen and the zinc chloride are equal, for only hydrochloric acid and zinc sulphide are initially present. The result is expressible by taking the volume V, in which a known amount of hydrochloric acid was dissolved, as the initial concentration; and the fraction x to denote that portion which after contact with zinc sulphide has finally reacted, forming zinc chloride. Hence we have

$$3{\cdot}96 \log \frac{1-x}{V} - 3{\cdot}57 \log \frac{x}{V} = \text{const.};$$

and also

$$\frac{x}{(1-x)^{1{\cdot}11}} V^{0{\cdot}11} = \text{const.}$$

This function is really nearly constant:

Volume (V).	Portion reacted (x).	$\frac{x}{(1-x)^{1{\cdot}11}} V^{0{\cdot}11}$.
1	0·0411	0·043
2	0·038	0·0428
4	0·0345	0·0418
8	0·0317	0·0413

Similar experiments with sulphuric acid, where i for H_2SO_4 and $ZnSO_4$ is respectively 2·06 and 0·98, gave

$$\frac{x}{(1-x)^{1{\cdot}02}} V^{0{\cdot}02} = \text{const.};$$

and here also x is nearly a constant, as is seen from the following experimental numbers:—

Volume V.	Portion reacted (x).
2	0·0238
4	0·0237
8	0·024
16	0·0241

5. The experiments of Engel on the solubility of magnesium carbonate in water containing carbonic acid (*Comptes rendus*, c. pp. 352, 444) also deserve notice. The state of equilibrium is

$$MgCO_3 + H_2CO_3 \rightleftarrows Mg(HCO_3)_2;$$

and our formula leads to the following relation, where $i = 2{\cdot}64$ for acid magnesium carbonate:—

$$0{\cdot}379 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

The number found was

$$0{\cdot}370 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

6. Other experiments by the same author on the simultaneous solubility of copper and ammonium sulphates (*Comptes rendus*, cii. p. 113), are shown by the reversible equation

$$CuSO_4 + (NH_4)_2SO_4 \rightleftarrows Cu(NH_4)_2(SO_4)_2.$$

As the double salt was always partly undissolved, and as the values of i for $CuSO_4$ and for $(NH_4)_2SO_4$ are 0·98 and 2·0, we have the relation

$$0{\cdot}49 \log C_{CuSO_4} - \log C_{(NH_4)_2SO_4} = K.$$

The number found is $0{\cdot}438 \log C_{CuSO_4}$.

7. In conclusion, we may notice Le Chatelier's experiments on the equilibrium between basic mercuric sulphate and sulphuric acid (*Comptes rendus*, xcvii. p. 1565);

$$Hg_3SO_6 + 2H_2SO_4 \rightleftarrows 3HgSO_4 + 2H_2O.$$

In this case the values of i for H_2SO_4 and $HgSO_4$ are 2·06 and 0·98, and we have

$$1{\cdot}4 \log C_{H_2SO_4} - \log C_{HgSO_4} = K.$$

The found value is $1{\cdot}58 \log C_{H_2SO_4}$.

Generally speaking, therefore, such results show a very satisfactory agreement.

Prof. Rücker regretted that the names Boyle's Law and Gay-Lussac's Law had been so persistently made use of in the paper, as he thought a wrong impression would be spread as to the nature of the phenomena. He also considered it probable that the proportionality observed was merely the result of the smallness of the ranges over which the experiments had been made. Mr. H. Crompton took exception to the imaginative character of the reasoning, and thought much more experimental proof was required before the results could be accepted for any but very small ranges of concentration. In answer to Prof. Reinold, Prof. Ramsay said the experimental data were not obtained by Van't Hoff himself, but were taken chiefly from Raoult's determinations.

XLV. *Experiments on Electrolysis.*—Part II. *Irreciprocal Conduction.*

By W. W. Haldane Gee, *B.Sc., Lecturer of the Victoria University, and* H. Holden, *B.Sc., Bishop Berkeley Fellow in Physics, of the Owens College, Manchester* *

[Plate X.]

We have observed, when strong sulphuric acid is used as an electrolyte, the electrodes being of platinum, that the decomposition nearly ceases, if by decreasing the resistance in circuit we attempt to increase the current beyond a certain maximum. An investigation of this curious behaviour has shown that it may best be included with the miscellaneous phenomena grouped under the head of *unipolar*, or, as it may better be called, *irreciprocal* conduction †. The early experimenters in voltaic electricity devoted much attention to this subject, and it will be desirable to give some account of their labours before proceeding to describe our own experiments.

Section A. Historical and Critical.

1. *Experiments of Erman.*

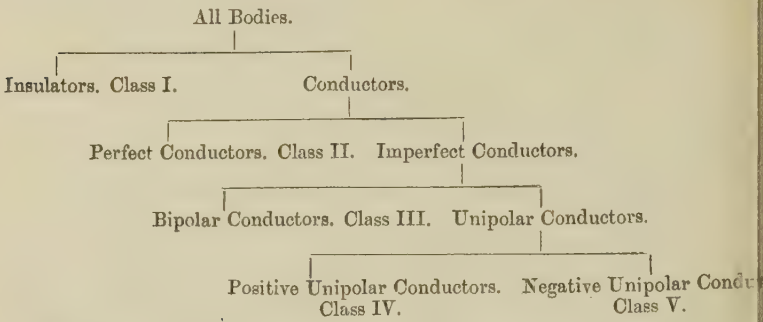
Among the many papers in the earlier volumes of Gilbert's *Annalen der Physik*, which the invention of the voltaic pile had directly inspired, will be found several by Prof. Erman of Berlin. With the aid of the imperfect instruments known at that time he made an investigation on the conducting

* Read May 26, 1888.

This is the second of a series of papers on Electrolysis and Electrolytic Polarization, descriptive of experiments made since January 1887 at the Owens College Physical Laboratory. An abstract of the experiments made, to the end of August 1887, was submitted to the British Association meeting at Manchester. We desire to acknowledge the assistance received up to that time from Mr. C. H. Lees, B.Sc., Derby Mathematical Scholar of the Owens College. His cooperation has since been discontinued, owing to absence at Strasburg.

† Following Christiani's use of the term, irreciprocal conduction is said to occur if a reversal of the *direction* of a current causes any change in its *magnitude*.

power of bodies; and in his fourth research* there appears a division of bodies into five classes, of which the following schema shows the chief features :—



To understand this classification it will be necessary to describe the method of experiment employed by Erman in order to find the class to which a body belonged. PN (Pl. X. fig. 1) is a well insulated Volta's pile, P and N being the positive and negative poles respectively. Connected with P is a gold-leaf electroscope E and with N a similar electroscope E_n. The body (B) to be tested, which is permanently connected with earth, is made to touch separately E_p and E_n. If the body belongs to Class I. neither of the electroscopes will be affected, but the case is otherwise if B is a conductor. Let us suppose the latter; it will, therefore, be necessary to ascertain to which of the other four classes the body belongs. Permanent connexions are made (as represented by the dotted lines of fig. 1) with B, and the behaviour of the electroscopes is carefully noted. If there is a sudden and complete collapse of the leaves of both E and E_n, the body belongs to Class II.†; if, on the other hand, both E_p and

* "Ueber die fünffache Verschiedenheit der Körper in Rücksicht auf galvanisches Leitungsvermögen." Gilbert's *Annalen der Physik*, Band xxii. S. 14 (1806).

† The following extract from Erman's paper (*loc. cit.* p. 18) is interesting, as evidence of his scientific caution:—"The distinction between perfect insulators and perfect conductors was perceived very early with the battery, and though it may indeed be believed that no important discoveries remain to be made in this matter, it is very desirable not to consider the matter as fully settled, for it is possible that also here important modifications of conductivity lie hidden. For example, it has really not

E_n are partially discharged, B is placed in Class III. If E_p alone is discharged, B is a positive unipolar conductor; if this is the case only with E_n, B is a negative unipolar conductor.

At the time when Erman classified conductors in this manner Ohm's law was not known, hence the behaviour of the electroscopes under these conditions could not be thoroughly appreciated. However, it was recognized that in the cases of Classes IV. and V. there must be a high resistance at one of the contact points n or p, preventing the conduction of the charge of E_n or E_p to earth.

It was found that well-dried soap was a good example of Class V. Hence Erman studied the unipolar conducting-power of soap in some detail, but he was unable to come to any definite conclusion why at p there should be a very high resistance. He rejected, on grounds which need not here be described, the hypothesis of an insulating film composed of the decomposed soap-acids *.

Interesting examples of Class IV., Erman found, are furnished by flames. Their anomalous conductivity yet remains but imperfectly explained †.

2. *Experiments of Ohm.* (a) *On Soap.*

Ohm ‡ confirmed the experiments of Erman, and came to the conclusion that the cause of the high resistance at the anode was due to a layer of fatty acids.

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yet been proved whether, with the so-called perfect conductors, there are not degrees of conductivity. Thus, though it is usual to regard all metals as equally good conductors, I should like this law not to be so unconditionally assumed, before direct measurements have proved its generality. Indeed, who knows whether finally with each metal certain properties will not be made apparent, which in respect to galvanic electricity are analogous to those which so excellently characterize iron, nickel, and cobalt with regard to magnetism?"

* *Loc. cit.* p. 50.

† The conducting power of flames has been studied by Ritter, Hittorf, Andrews, Hankel, Braun, Fuchs, Macfarlane, Rintoul, and others.

‡ Schweigger's Journal, lix. (1830) p. 385.

(b) *On Sulphuric Acid and Caustic Potash.*

Ohm* employed a galvanometer in studying the unipolar conductivity of these liquids. The instrument was placed in series with 1–6 single fluid zinc-copper cells, and a voltameter containing strong sulphuric acid. Employing electrodes of platinum, gold, silver, copper, iron, lead, and tin, he found that the deflection obtained on first making the circuit speedily sank to a very small amount. He showed that the cause diminishing the current was between the anode and the acid; for on bridging across the anode and the liquid by some moist threads the deflection was immediately increased to the original amount. Also, in the case of the oxidizable metals, by diluting the liquid in the neighbourhood of the anode the current was greatly increased, whilst a dilution of the liquid near the kathode produced no effect. Further, replacement of the anode by a clean electrode produced the original deflection for a time, whilst changing the kathode made no difference. He finally concludes that the fall of the current is due to the development of a force at the anode. This conclusion he verified by the use of an electroscope. Thus strong sulphuric acid is classed amongst the negative unipolar conductors †.

Ohm also experimented with various electrodes in strong potash solution, which led him to regard the latter as a positive unipolar conductor.

3. *Experiments and Theory of Christiani.*

The only modern contribution of importance to the subject of irreciprocal conduction is the pamphlet ‡ produced by the

* Schweigger's Journal, lx. (1830) p. 32.

† It seems probable that what Ohm observed was a decrease of current due—(1) in the case of the oxidizable electrodes to a transition resistance caused by the formation of a badly conducting salt-layer on the anode in strong sulphuric acid; (2) in the case of platinum and gold in sulphuric acid and potash solution to polarization, this polarization being of a unipolar nature, that is to say it was much greater at one electrode than at the other. We do not believe that Ohm ever observed the phenomenon of unipolarity in strong sulphuric acid with electrodes of platinum or gold due to a transition resistance. This conclusion is supported by comparing Wiedemann, *Electricität*, Bard ii. pp. 629, 657.

‡ *Ueber irreciproke Leitung electrischer Ströme.* Berlin: Friedländer und Sohn (1876). Contains 174 pages and 1 plates.

late Prof. Christiani, whilst working in the laboratory of Du Bois Raymond. He investigated generally the case of electrolysis with unequal-sized electrodes, and comes to the conclusion that, as a rule, with low E.M.F.'s the current is able to pass more easily from the lesser to the greater electrode, and *vice versâ* with large E.M.F.'s. This difference, he says, exists after the influences of polarization and chemical transition resistance are allowed for, meaning by the latter term a resistance due to the products of electrolysis. We have been at some trouble to examine the experiments and reasoning upon which the above conclusion is based, and have arrived at the opinion that they are equally open to criticism; his results and theory being, however, very interesting and representing a large amount of work, it will hence be desirable to notice them at some length, especially as his pamphlet is not readily accessible in England.

In order to eliminate as much as possible changes in the electrolyte caused by the passage of the current, momentary currents from an induction-coil were used throughout the greater part of his work, his object being a study of the nature and causes of irreciprocal conduction, with unequal-sized electrodes, in electrolytes. For this purpose, applying a momentary E.M.F. to the voltameter, he desires to measure:—

(*a*) The quantity of electricity which is sent through the voltameter by this E.M.F., and (*b*) the polarization which opposes its passage.

Fig. 2 shows the essential parts of the arrangement used with induced currents. V is the voltameter with a platinum plate and a platinum Wollaston's point as electrodes. In circuit with it are a dead-beat Wiedemann's galvanometer (G) and the secondary coil (S) of an induction-coil, of which P is the primary coil in circuit with a battery. By changing the distance of S from P ($=x$), the E.M.F. of the induced current can be varied. The experiments were conducted somewhat as follows:—By opening the primary circuit a quantity of electricity ($=q_1$) is sent through the voltameter, and the kick ($=k_1$) on G is noted. If the deflection does not return exactly to zero, but goes on the other side of it, this negative deflection ($=e_1$) is observed, and afterwards, in discussing the possible causes of irreciprocal conduction, is taken

as a measure of the polarization opposing the passage of q_1. The same induced E.M.F. is now, by reversing the voltameter terminals, applied in the opposite direction. Let k_2 and e_2 be the deflections now obtained, and suppose that q_2 is the quantity of electricity sent through the voltameter in this direction of the current. The distance of S from P is now altered, generally by 5 millim. at a time, and at each new position the above procedure is repeated, giving values of k_1 and k_2 for each value of x. He finds that k_1 and k_2 are generally different, but for *one* value of x they are equal; for values of x below this, one of them is the greater; for values of x above this, the other is the greater. He then assumes that k_1 and k_2 are proportional to q_1 and q_2 respectively, and thus proves the existence of irreciprocal conduction.

The assumptions made, namely (1) that e_1 is a measure of the polarization E.M.F. which opposes the passage of q_1, and (2) that k_1 is exactly proportional to q_1, do not seem to be admissible. Firstly, with regard to (1), e_1 is really proportional to the depolarization current which exists a certain time, conditioned by the time of vibration of the galvanometer &c., after the charging E.M.F. has ceased, and is not proportional to the value of the polarization E.M.F. during the existence of the charging E.M.F., unless the rate of depolarization is constant, which it usually is not. Also, as will be shown in a subsequent paper, the rate of depolarization with unequal-sized electrodes depends on the direction of the charging current. It may also be noticed that q_1 or q_2 &c. do not necessarily bear any simple relation to the value of the induced E.M.F. The quantity of electricity which passes in any time dt during the existence of the induced E.M.F. is proportional to the difference between the values at that time of the induced E.M.F. and of the polarization ; and therefore the relation between the charging E.M.F. and the quantity of electricity which passes during its existence depends on the rate of increase of the polarization E.M.F., which can scarcely be said to be known, but is probably not constant, and may even vary according to the direction of the current. The validity of assumption (2) is also doubtful, for the kick (k) on the galvanometer depends not only on q (the quantity of electricity which passes during the existence of the induced

E.M.F.) but also on the magnitude of the depolarization current, since the duration of the induced E.M.F. is certainly over before the galvanometer-needle has moved from zero to k divisions. Thus it would seem that k is only at best, in the case of non-polarizable electrodes, an approximation to the value of q; and therefore Christiani's numbers are not sufficiently trustworthy to serve as foundation for an elaborate theory.

Christiani, however, assumes that k and q are exactly proportional and plots curves * giving the relation between q and the induced E.M.F. in the two directions of the current. The point of intersection of the two curves is called the reciprocal point; its abscissa being proportional to the induced E.M.F., which gives equal kicks in the two directions, and its ordinate equal to these kicks. The conditions for the occurrence of reciprocity are then investigated. He finds (1) that lessening the size of the point electrode causes reciprocity to occur with lower E.M.F.'s, but that fairly large changes in the size of the plate electrode or in the distance of the electrodes have not much influence; (2) that decreasing the temperature causes reciprocity to occur with lower E.M.F.'s; and (3) that the degree of concentration of the solution is of influence. A discussion of the possible causes of irreciprocal conduction follows. Polarization, he says, cannot be the cause of irreciprocity, because he has obtained the latter with non-polarizable electrodes. Further, some measurements of the polarization by a wippe method show, as far as such a method is satisfactory †, that polarization is not the main cause of irreciprocity. His arguments against polarization, based on the measurements of e_1 (see p. 339) are, as before explained, of no value. His main argument against a chemical transition resistance is the following experiment :—A solution of potassium iodide is taken, and a certain number of currents sent through until the E.M.F. is found for which reciprocity occurs; the electrodes are then taken out and cleaned, and fresh solu-

* These curves are regular and never intersect in more than one point, and with some electrolytes do not intersect within the limits of experiment.

† The values of the polarization obtained by this method are of course open to the objection that they depend on the rate of fall of polarization after the removal of the charging battery.

tion used. The same E.M.F. is now again applied, and it is found that reciprocity still occurs; or, in other words, changes in the electrolyte caused by the passage of previous currents do not affect the value of the E.M.F., for which the momentary currents are the same in the two directions. The direction in which the E.M.F. is first applied is also quite indifferent. He remarks, however, that the reciprocal point in other electrolytes is, to some extent, affected by the passage of previous currents.

Christiani to a small extent makes use of permanent currents, but only in the case of the so-called non-polarizable electrodes. The following specimen of his results, with amalgamated zinc electrodes in concentrated zinc sulphate, will indicate their general features :—

1st Experiment.—Plate electrode $= P_p = 37 \times 26$ millim.
Point electrode $= P_s = \frac{1}{2}$ size of P .

Seconds after making circuit.	Deflections.	
	P_s+.	P_s-.
0	217	217·5
120	Begins to fall.	
600	45, vibrating.	220

2nd Experiment.—P_p = same size as before. $P_s = \frac{1}{4}$ size of P_p

Seconds after making circuit.	Deflections.	
	P_s+.	P_s-.
0	188·0	196·0
40	Begins to fall.	
180	14·0, vibrating.	
600		196·0

Here it seems evident that the irreciprocity is due to th

gradual formation of a badly-conducting film on the anode, but Christiani does not accept this simple explanation, apparently because it would not, as he thinks, explain the results obtained with transient currents.

Having rejected both polarization and a chemical transition resistance as causes for the effects obtained, a theory of electrolysis which would afford an explanation of them was necessary. The theory which Christiani evolves is a direct development of the idea that electrolysis is a convection of electricity by the atoms of matter. He considers the mechanism of electrolysis to consist in the two ions of a molecule conveying equal and opposite quantities of electricity in opposite directions, but assumes (1) that *the impulse causing this motion takes place only at the anode.* He assumes, moreover, (2) that in a given electrolyte the number of atoms ($=n$) which meet any unit area in unit time only depends on the temperature of the electrolyte. Finally, he makes use of the assumption (3) that every monad ion carries the same quantity of electricity ($=e$). These assumptions are applied finally to the case of unequal-sized electrodes, a plate of area P and a point of area S, as follows. According to assumption (2) the number of atoms which touch the plate in unit time will be nP, and therefore by (3) the greatest quantity of electricity which can leave the plate by ordinary convection in unit time is nPe, and similarly nSe is the greatest quantity of electricity which can leave the point in unit time. He then argues that, although n is a very large quantity, e is a very small one, and that it may thus happen that nPe and nSe are quantities of electricity small enough to be dealt with in experiment. He then considers the effect of an E.M.F. ($=$E) acting in the circuit for a very short time ($=t$). Suppose that the plate is the anode and let such an E.M.F. ($=\mathrm{E}_p$) be applied for a very short time ($=t$) that the quantity of electricity which passes is equal to nPet. In this case, when the E.M.F. applied is just sufficient to charge the nPt atoms which appear at the plate anode during the time t of charge, Christiani says, from energy considerations, that the most favourable conditions for the passage of the electricity are attained, or, in other words, the resistance of the cell is now a minimum. If the E.M.F. applied be less than E_p the resistance of the cell

increases because all the atoms which touch the anode are not engaged in carrying the electricity; if, on the other hand, an E.M.F. greater than E_p is used, the resistance of the cell again increases because a process analogous to spark-discharge has to go on. Similarly, if the point is the anode, there will be a certain E.M.F. ($=E_s'$) for which the resistance of the cell, for the direction of the current, is a minimum $\left(=\frac{E_s}{nSe}\right)$. Let the E.M.F. actually applied be E, there are then three cases possible. Since $E_s < E_p$,

(1) $E < E_s < E_p$, (2) $E_s < E < E_p$, (3) $E_s < E_p < E$.

Now, according to Christiani, the resistance of the cell is greater or less (*i. e.* an additional *electrical* transition resistance is greater or less) according as the E.M.F. applied is more or less different in value from that giving the minimum resistance. Thus in case (1), where E is nearer to E_s, the quantity of electricity which passes will be greater if the point is the anode. In case (2), where E is between E_s and E_p, there will be one value of E which will give equal quantities of electricity in either direction of E. In case (3), where E is nearer to E_p, the quantity of electricity will be greater if the plate is the anode.

The theory is thus highly ingenious, but its verification is a matter of considerable difficulty, for we have to distinguish the effects of polarization and *chemical* transition resistance from the *electrical* transition resistance. As we have pointed out, Christiani's own results are open to doubt, so that unless some better method of experiment can be suggested the hypothesis of Christiani must remain but an interesting speculation.

Section B. Descriptive of our Experimental Work.

1. *Arrangement of Apparatus.*

We have found the arrangement shown in fig. 3 very convenient for the larger part of our experimental work.

M is a battery consisting usually of from 1 to 6 secondary cells;

k_1 is a commutator for reversing the main current;

k_2 is a four-way plug-key enabling the voltameter-circuit to be broken or short-circuited, or cut out of the circuit altogether;

V is the electrolytic cell;

G is a dead-beat Deprez and D'Arsonval galvanometer;

k_3 is a commutator used to reverse the current through G;

k_4 is a switch hinged at E. According as the contacts D and A *or* those at C and B are made, then (1) the battery is included *or* excluded from the voltameter-circuit, (2) the low-resistance galvanometer-shunt S_p *or* the high resistance galvanometer-shunt S_s is in use, and (3) the resistance-box R_p *or* R_s is employed. The switch k_4 enables us, therefore, to study the changes of current-intensity when the electrolytic cell is in circuit with the battery, and also the changes of the polarization-current which ensue after cutting the battery out of the circuit.

2. *Experiments with strong* H_2SO_4 *and* Pt *Electrodes.*

a. *General description of the Phenomenon to be observed.*—In the opening paragraph of this paper it was stated that, through a given voltameter, consisting of Pt electrodes in strong H_2SO_4, currents of an intensity below a certain maximum could alone pass, and that if we tried to increase the current strength above this maximum, it was found that the deflection on a galvanometer in circuit diminished nearly to zero, and that decomposition nearly ceased. Further investigation soon showed that the size of the electrodes was also of great influence in determining the stoppage of the current, as is well shown by the following arrangement (see also Table I.). Take two clean platinum electrodes, *one being much larger than the other*, and place them in strong pure H_2SO_4. It will be found that a very large current can pass from the larger to the smaller electrode (see fig. 4, α direction of current), giving a deflection say of several hundred divisions on the galvanometer. On reversing the current (see fig. 5, β direction of current), if it be of suitable strength, after the first sudden deflection the galvanometer-needle will soon return nearly to zero; in many cases scarcely a trace of a deflection is to be observed; in fact the current in the α direction may be more than a thousand times as great as that

obtained in the β direction on reversing k_1. We desire to ascertain the cause of this (almost total) stoppage of the current, and to study generally the conditions determining its occurrence; and in connexion with this, it may be noted that the formation of a sheath of gaseous bubbles round the anode always attends this stoppage of the current with Pt electrodes.

b. *Experiments proving Existence and Locality of an Insulating Film.*—If, after the production of the insulating condition, we replace the kathode by a *large* electrode the current is still stopped, but if the anode be similarly exchanged the current passes readily. This experiment proves that there is some obstructing cause at the anode. To determine its nature attempts have been made to measure the polarization and resistance of the cell in the α and β directions. Operating very rapidly with the dead-beat galvanometer, and using Ohm's method, we find that the resistance in the β direction (after the insulating condition is produced) is very much greater than in the α direction. Thus in one experiment the resistance in the α direction was only 10 ohms, whereas on reversal it rose to 10,000 ohms, and continued to increase for some time after the insulating condition was produced. The polarization, on the other hand, may be regarded as equal in the two directions, for, using a compensation method in which the voltameter-circuit was momentarily opened, and the polarization balanced against a known E.M.F., we have found 2·5 volts to be the value both when the insulating condition was produced, and also when it was not. This result was confirmed by Ohm's method. Thus the polarization is not abnormal, and therefore cannot be a determining factor in producing the insulating condition. Such a conclusion was from the first to be expected, as the stoppage of the current had been produced when a battery having an E.M.F. of ten volts and upwards had been employed. Measurements of the resistance were also taken by Kohlrausch's method, this being done by breaking the circuit of fig. 3 between a and b, and including the arrangement in one of the arms of a Wheatstone's bridge. It was found very difficult to get anything but a very approximate value of the resistance during the insulating condition, for the passage of the alternate currents

apparently tended to destroy the insulation, and caused continual vibration of the needle of the dead-beat galvanometer. This effect was much less when the current was sent in one direction through the primary coil of the induction-coil than in the other. The values of the resistance obtained, however, fully confirmed those obtained by other methods; so that we may conclude that the insulating condition is due to a resistance at the anode. In what follows it will be convenient to regard this as due to a film of badly-conducting matter.

c. *The Film-forming Current-density.*—If we increase the size of the anode a greater current is necessary to produce the insulating condition, hence the current-density at the anode is an important factor in determining the formation of the film (see Table I.). Calling C the minimum current which will form the film and S the whole surface of the anode immersed, then $C/S = \Delta$ we shall define as the *film-forming current-density*. The actual value of Δ depends upon several conditions, such as will be best understood after an examination of Tables I. and II.

Examination of the following and similar observations show that Δ is not perfectly definite in value, but is greatly influenced by the previous treatment of the anode. For example, if the anode has been heated to redness and washed before putting in the current, the film forms with a less value of Δ than if the anode had been previously used for electrolysis (see experiments 2 and 3, Table I., and 5, 6, 7, and 21, Table II.). Generally speaking, previous currents in either direction cause Δ to increase, but after the current has been on for some time in the β direction, a reversal for a short period seems to assist the formation of the film. Experiment 6, Table I., shows very markedly the effect of unclean electrodes. It is noteworthy that, when the current-density in the β direction is at first of a value Δ' greater than Δ, the rapidity and completeness of the film-formation depends upon $\Delta' - \Delta$.

TABLE I.—Showing Effect of (1) Size of Anodes, (2) Previous history of Electrodes.

k = constant of galvanometer = ·000365 ampere.
S = surface of anode = $l \times$ ·06 sq. cm. approximately.
l = length of anode.

The electrodes used were of platinum, one of them being a plate 40 millim. × 8·5 millim., the other a wire ·2 millim. diameter, whose length was varied during the experiment. These were placed in strong pure H_2SO_4, and a battery with an E.M.F. of 6 volts employed.

Remarks.	l.	C.	Δ.
	mm.	ampere.	ampere per sq. cm.
1. Had been passing current a long time in β direction	20	k 287 = ·105	·87
2. Ditto	10	k 140 = ·0511	·85
3. Washed and heated electrodes	„	k 100 = ·0365	·61
4. Current on in α direction for 15 seconds	„	k 90 = ·0328	·55
5. Ditto for 60 seconds	„	k 92 = ·0335	·56
6. Wiped electrodes with paper. Shows influence of unclean electrodes	„	k 240 = ·0876	1·46
7. Washed and heated electrodes	„	k 110 = ·0402	·67
8. Current on in α direction for 30 seconds	„	k 150 = ·0547	·91
9. Ditto for 45 seconds	„	k 120 = ·0438	·73
10. Broke circuit; lifted electrodes up and down in the liquid several times. Film evidently not thoroughly removed by this process, and therefore easily reformed	„	k 70 = ·0255	·43
11. Broke circuit; lifted electrodes out of liquid for 10 seconds, then moved them up and down in liquid for 30 seconds	„	k 130 = ·0475	·79
12. Mixed treatment	5	k 63 = ·0230	·77
13. Current on in α direction for a moment	„	k 67 = ·0245	·82

The resistance of the voltameter was, as estimated by Ohm's method, 45 ohms in the α direction of the current, and 4500 ohms in the β direction when the film was formed. Increasing the E.M.F. of the battery made no difference in the value of C.

TABLE II.—Showing Effect of (1) Change of Current-strength, (2) Previous history of Electrodes.

k = constant of galvanometer = ·00051 ampere.

The electrodes were of platinum, size not noted, and the electrolyte was strong pure H_2SO_4.

Treatment of Electrodes.	Ohms in circuit with voltameter.	Deflection.	Remarks.
1. (During experiments	30	117	Deflection steady.
2. 1–7 the current	20	162	„ less steady.
3. was kept continu-	15	191–194	Vibrations more marked.
4. ously on in the	10	235–238	
5. film-forming (β) direction.)	5	315–321	Vibrations, which were not regular.
6.	3	365–370	„ „ „
7.	0	4	Film formed; the deflection being reduced immediately to 4.
8. Short-circuited voltameter for a time.	3	4	„ „ „
9. Current reversed for an instant	3	4	„ „ „
10. Electrodes heated to redness	3	4	„ „ „
11. Short-circuited voltameter for a time.	6	4	„ „ „
12. „ „	10	212	
13. Current reversed for an instant	9	230–234	
14. „ „	7	235–250	
15. „ „	6	250–20	Film formed; deflection reduced to 20.
16. „ „	5·5	270–20	Deflection at first 270, then fell gradually to 150, and then a rapid fall to 20.
17. Electrodes reheated .	5·5	220–20	Deflection fell gradually to 20.
18. Current reversed an instant and then voltameter short-circuited	6	270–300	
19. „ „	5·5	275–310	
20. „ „	5·5	280–300	
21. Electrodes reheated..	5·5	200–4	
22. Current reversed an instant and then voltameter short-circuited	5·5	270–310	
23. Electrodes reheated and allowed to stand 5 minutes in the acid	5·5	4	Film quickly formed.

The method of placing the anode in the acid has an important influence upon the value of Δ, as the following experiments show:—

Exp. I.—The end of a Pt wire used as an anode was immersed in the acid, and then the film was formed by the lowest value of the current-density. The anode was then *gradually* lowered into the acid, when it was noticed that the film was formed over the whole wire. When the wire was lowered *rapidly* the film remained on the lower part for a time, but the upper portion was conducting, as evidenced by the escape of gas from it.

Exp. II.—The reverse of the previous experiment is not easy to perform. If we have at first the whole length of the wire immersed and use a current-density just less than Δ, and then try to form the film by diminishing the length of the wire immersed—the strength of the current meanwhile being kept constant—it is difficult to do so.

d. *Persistence of Film.*—The disappearance of the film was generally tested for by means of a weak current as follows:—Knowing what deflection would be obtained, when the film was not formed, with a certain large resistance in circuit, then after the film had been formed the resistance was increased to this value: if the current corresponding to this resistance without the film was able to pass, it showed that the film had been totally removed, and generally, from the amount of current which did pass, could be estimated the degree of disappearance of the film.

After the formation of the film there are no signs of its disappearance as long as the battery is left in circuit with the voltameter, but if the circuit be broken the film tends to disappear, the rate of disappearance depending on the completeness with which the film had previously been formed. It disappears very quickly if the voltameter be short-circuited, and instantaneously if the current be reversed.

The film is removed at once if the anode be taken out of the liquid and wiped, but if the anode be left in the liquid—the electrodes being still in connexion with the battery—the anode may be moved about in the liquid or rubbed with a glass rod without destroying the film. If the rubbing be

vigorous the film will be partially destroyed, but on ceasing the friction the film immediately reforms. The anode may be removed from the liquid and held in the air some time without thoroughly destroying the film. When in the liquid a stream of air-bubbles may be blown violently against the anode without destroying the film, but if the anode is removed from the liquid a moderate current of air blown against it removes the film.

Vibrating the anode, when the film is on the point of being formed, certainly helps its formation, but after the film has formed violent agitation does not affect it, though by this means the outer layers, at least, of the sheath of bubbles round the anode may be removed. We have tried the effect of mounting the voltameter on a whirling table, the electrodes being kept fixed, and find that we can form the film when the voltameter is rapidly rotating. The value of Δ with the rotating voltameter was little, if any, different from that obtained when it was stationary. Touching the anode with an iron wire immediately destroys the film; this is also the case if a platinum wire is used to touch the anode, but when the platinum wire is not too large the film reforms.

According to our measurements the E.M.F. of polarization is about 2·5 volts; if after the film has been formed we reduce the battery E.M.F. to a value rather less than this without breaking circuit, we find that the film disappears more slowly than if the circuit is broken.

e. *Influence of Degree of Concentration of Acid.*—A small percentage of water appears to exercise but little influence on Δ, but when the liquid contains as much as 70 per cent. water by volume we have been unable to produce the film. The general effect of dilution is exhibited in the following table; the variations of Δ for percentages of acid between 98 and 87 being probably due to accidental causes. The dilution seems also to diminish the rate at which the film is formed.

TABLE III.—Showing Effect of Concentration.

A. Impure H_2SO_4. Temperature 9°·2 C.		B. Pure H_2SO_4.		
Percentage of acid by vol.	Relative values of Δ.	Percentage of acid by vol.	Temperature.	Relative values of Δ.
98	248	70	+11° C.	25
97	273	60	+13°·5 C.	62
96	272	50	+14°·3 C.	150
95	272	40*	+15°·8 C.	500
93	242	30	−10° C.	No film.
90	250			
87	250			
82	340			
78	360			

f. *Influence of Temperature.*—Inspection of the curves (figs. 6, 7, and 8), giving the variation of the film-forming current-density with the temperature will show that Δ is markedly affected by a change of temperature, and particularly so at the higher temperatures; an increase in the temperature requiring a corresponding increase in Δ, the rate of increase of Δ with temperature being greater at the higher temperatures. The observations from which the curves are drawn were obtained in the following manner:—The anode and kathode were placed in separate beakers, each containing strong pure H_2SO_4. Connexion was made between the two vessels by means of several inverted U-tubes filled with acid. The beaker containing the kathode was kept at a constant temperature throughout. Starting with both beakers at about 15° C. the current was put on in the β direction, and the current-resistance varied until the film was formed and the corresponding value of Δ noted. The current was then reversed for a moment in order to remove the film, the beaker containing the anode heated, and for every few degrees of rise of temperature Δ was found as just described. In the case of falling temperatures the process was somewhat different and yielded more regular results.

* The production of the film in acid of this degree of dilution effectually disposes of any idea that hydroxyl can have any influence in forming the film. See footnote of our former paper, *ante*, p. 160.

After Δ had been found for the highest temperature, the resistance in circuit was slightly increased, the film being removed by reversing for an instant, and the anode vessel allowed to cool. The temperature was then noted at which the film again formed with the slightly diminished current. This procedure was repeated until the anode vessel had cooled down to the desired extent.

g. *Influence of Viscosity.*—It was thought probable that if we made dilute H_2SO_4 (say 10 per cent. acid) sufficiently viscous that the film would be produced ; but negative results have accompanied the addition of both glycerine and gelatine to the dilute acid. With a 50 per cent. acid to which 2 per cent. of gelatine had been added, the value of Δ was reduced to one third by this addition. Addition of glue to strong H_2SO_4 has a similar effect in lessening the value of Δ *.

h. *Effect of Platinizing the Electrodes.*—Some difficulty has been experienced in trying to estimate the effect which platinizing a platinum electrode has on the value of Δ, on account of the impossibility of accurately measuring the surface of the platinized wire. There is no doubt that after platinizing a few moments much greater *currents* than that which produced the film before platinization are now unable to do so, but whether the surface of the anode has increased by platinizing in the same ratio we are unable to say. In one case, in which before platinizing the film was formed with a current of 70 divisions, after a few moments' platinizing the film would not form with currents as high as 300 divisions

3*a*. *Experiments with* H_2SO_4 *and Carbon Electrodes.*

In these experiments we at first found considerable difficulty owing to the disintegration, during electrolysis, of the various kinds of carbon. Carré-prepared carbons, gas-carbons, and graphite (from lead-pencils) all behaved in the same way. On making circuit no gas at first comes from the anode, but

* It is perhaps worth mentioning that a jelly made of glue and water gave the film at the kathode. In one case, when the electrodes were a wire and a Wollaston's point, the resistance was 2000 ohms when the wire was kathode, and 45,000 ohms with the point as kathode.

eventually the outer shell breaks off and gas is evolved*. It occurred to us that the coherent carbon filaments used in incandescent lamps might be free from this objection, and this conjecture was found to be justified. At first filaments from Swan lamps were used, and afterwards some kindly supplied by Messrs. Woodhouse and Rawson. With either of these carbons we were able to electrolyze strong H_2SO_4 without any disintegration or coloration of the liquid.

Using these carbon filaments we were able to readily produce a film at the anode which had the same general properties as that obtained with platinum. To make sure that the film was not due to any coating of oxidizable material the filaments were boiled in aqua-regia and well washed, but this had no influence in preventing the formation of the film. Platinized carbon behaves as regards the film-formation exactly like platinized platinum. The insulating condition, with carbon filaments, is accompanied, as in the case of platinum, by the formation of a gaseous sheath round the anode.

3 *b*. *Experiments with* H_2SO_4 *and Gold Electrodes.*

Some fine gold wire, sold to us as pure by Messrs. Johnson, Matthey, & Co., and a piece of platinum foil were used together as electrodes in strong pure H_2SO_4; the platinum and gold being placed in separate limbs of a U tube. The behaviour of this combination was very peculiar. The film readily formed when the gold was anode, but no sooner had it formed than it began to disappear again, and did not reform until the circuit had been broken. On making the gold wire the anode, after the current had been in the previous direction, it was noticed that one of two things happened, either (1) the deflection at first was large, and decreased rather quickly to a small value, then increased gradually to

* This behaviour of carbon has been noticed by Gore and others, and more recently studied by Debray and Pechard (*Compt. Rend.* cv. pp. 27–30). These observers, using gas and other kinds of carbon purified by Cl at high temperatures, found that the gas evolved at the anode during the electrolysis of H_2SO_4 was a mixture of CO_2 and O. The black powder formed on disintegration (after being washed and dried) deflagrated at a temperature below red-heat, evolving CO and CO_2.

its former value, or (2) the deflection at first was small and then made a sudden jump to a high value, at which it remained. The gold wire used was very rapidly eaten away.

4. *Experiments with other Electrolytes and Platinum Electrodes.*

a. *Phosphoric Acid.*—Efforts to produce a definite film have been unavailing. We have tried various solutions (including some quite viscous), and although we have found that there is a difference of deflection in the two directions of the current, the electrodes being a point and a plate, we are disposed to attribute this mainly to polarization. At the same time there certainly is evidence of a difference of transition resistance in the two directions, for in one case, using a battery E.M.F. of about 18 volts, the deflection when the point was anode was double that with the current reversed. This indicates that in the latter direction there is a higher transition resistance, for any difference of polarization in the two directions would probably be small relative to the E.M.F. employed.

b. *Caustic Potash.*—Different strengths of solution up to saturation, and a battery E.M.F. up to ten volts were used, but no definite film could be obtained. On adding glycerine to the solution, in order to increase its viscosity, the transition resistance, as measured by Ohm's method, was greater with the point anode than when kathode; in one experiment the resistances were 37 and 3·5 ohms respectively. Attempts were afterwards made to repeat the effects obtained by Ohm, with solutions of caustic potash, and for this purpose a battery of 3 Daniells was employed. The differences of the deflections in the two directions, and also the fall of the deflection obtained after making circuit, were generally to be attributed to polarization; but by using certain currents a tendency towards the formation of a transition resistance could be traced, as evidenced by the table below, the numbers of which were obtained by Ohm's method.

TABLE IV.—Irreciprocity with Platinum Electrodes in KHO *.

	Point anode.	Plate anode.
Resistance of voltameter, Exp. 1...	111·3 ohms.	33·5 ohms.
„ „ „ 2...	120 „	32 „
Polarization „ „ 1...	2·65 volts.	2·12 volts.
„ „ „ 2...	2·65 „	2·16 „
Current through „ „ 1...	·00265 ampere.	·0178 ampere.
„ „ „ „ 2...	·00247 „	·0149 „

c. *Other Liquids.*—No film was obtained with platinum electrodes in the following liquids :—(1) Pure fuming HNO_3; (2) a mixture of HNO_3 and H_2SO_4, the former being in excess ; (3) strong HCl; (4) a mixture of HNO_3 and HCl in equal parts. The film was obtained with strong H_2SO_4 in which CrO_3 had been dissolved, but no remarkable features were noticed.

5. *Experiments on Soap and Sodium Benzoate.*

A piece of common white soap was cut in the form of a cylinder 4 cm. long and 1 cm. diameter. It was protected by a glass tube, and mounted so that platinum plates pressed against its two ends. The resistance, as measured by Ohm's method, showed a gradually increasing value, the battery being kept, in circuit, from 1080 to 23,000 ohms, at which it remained constant. The polarization was taken for various times of charge, but showed but little variation. Measurements of the resistance of the soap with a battery in its circuit were also made by Kohlrausch's method, the results confirming those previously obtained by Ohm's method. With solutions of soap the solid soap acids were separated out, but there were no signs of any film-formation.

* Further measurements are being made both with KIIO and other liquids by means of the method of Fuchs, which with certain precautions now appears to us to be the one best adapted.

In many respects a solution of sodium benzoate resembles soap, for benzoic acid is but little soluble in water, hence it was thought that an electrolytic deposit at the anode might stop the current. This was found to be the case, different strengths of sodium benzoate giving the film without difficulty. Careful observation showed that with weak currents the oxygen produced at the anode was able to break through the layer of benzoic acid, and thus prevent the film-formation; but with strong currents the solid acid obtained the mastery, the oxygen then not being able to break through and so disperse the acid. Hence, with strong currents a film, consisting of solid benzoic acid in which oxygen bubbles were entangled, was formed round the anode, thus stopping the current.

6. *Discussion of the possible Causes of the Film.*

The film in H_2SO_4 with platinum electrodes is in many respects very analogous to those obtained in the same liquid with oxidizable electrodes, and also to that which causes the *passivity* of iron, in which cases a solid oxide or sulphate layer on the anode is acknowledged to be the cause of the insulation. The non-formation of the film with platinum electrodes in H_2SO_4 below a certain strength, the increase of Δ with the temperature, the fact that the film disappears gradually on breaking the circuit, and immediately on reversing the current, all point, it may be argued, to a solid oxide or sulphate layer on the platinum anode; the solubility of this layer varying with the concentration and temperature of the acid, and its disappearance being immediately caused by a deposit of nascent H on it. For although platinum is usually regarded as non-oxidizable, yet under the condition of electrolysis, which is attended by the production of ozone in quantity at the anode, it seems quite possible for an oxide of platinum to be formed. This view was strongly upheld by De La Rive. In his 'Electricity,' vol. ii. p. 410, he says that "the part played by platinum is very remarkable, for although it passes for being not oxidizable, yet it comports itself like the metals that are so, but in a feeble degree." The blackening of platinum electrodes in dilute H_2SO_4 caused by the passage of alternate or direct intermittent currents (the former being more effective) is

urged as a proof that platinum is attackable by the electrolytic gases. De La Rive insists upon the view that the blackening is due to a series of oxidations and reductions of the platinum, the oxidation with the direct currents being due to the O dissolved in the acid. Another view, mentioned by Wiedemann, is that the alteration of the surface is caused by the mechanical action of the hydrogen, which is first occluded and then evolved again from the electrode when the current is diminished or reversed. De La Rive gives other evidence in support of his theory of the successive oxidation and reduction of platinum, and explains the catalytic action of platinum according to this view. Schönbein, on the other hand, quite as firmly upheld the theory that the oxygen did not combine with the platinum, but formed a condensed gaseous film on its surface. Faraday also seems to have shared this view*.

Again, it should be mentioned that, using large current-densities, McLeod † found that very fine platinum wires were destroyed during the electrolysis of H_2SO_4 of density 1·3; but whether this was due to actual solution of the platinum or to its disaggregation or to traces of Cl is doubtful. If solution of the platinum really occurs, it would support the theory that the film is due to a solid oxide or sulphate layer, as in the case of the oxidizable electrodes. In this relation an experiment of ours may be quoted. A platinum wire was carefully cleaned and weighed, and then used as anode in strong H_2SO_4, the film being then formed on it. It was taken out quickly, and wiped (with asbestos), which, as said previously, removes the film. The anode was then replaced, the film again formed and again wiped off. This was repeated a great number of times, but no variation of the weight of the anode could be detected after the experiment, nor was there any difference in the appearance of the wire. We have further electrolyzed sulphuric acid with platinum electrodes continuously for many hours without finding any variation

* Exp. Res. vol. i. p. 165. It may be noted that Dulong and Thenard have shown in a research (*Ann. de Chim.* vol. xxiii. p. 440, 1823, and vol. xxiv. p. 380, 1823) that all bodies have the catalytic power, more or less.

† Journ. Chem. Soc. vol. xlix. p. 591.

in the weight of the electrodes. Negative experiments of this nature, however, cannot be regarded as having much value.

In endeavouring to ascertain the nature of the film we are met by the difficulty that removal from the acid speedily brings about the destruction of the film, and other evidences of its instability have been previously given. Thus, there is no possibility of applying the direct tests that have led to the generally accepted view in the case of the oxidizable electrodes, and although the film sticks with some firmness when in the electrolyte and the battery-current is not broken, yet there are no chemical tests which can be directly applied under these conditions that can be thought very satisfactory. We may, however, mention that the film remains undisturbed when a stream of hydrogen is passed in small bubbles over the anode, but is speedily removed if the acid round the anode be diluted by a stream of water. The formation of the film with carbon electrodes, the non-formation of the film with platinum electrodes in various oxidizing agents, and other minor properties, which will be found in the previous part of the paper, have led us to doubt the accuracy of the oxide theory in the case of platinum or carbon electrodes, and to *provisionally* adopt another theory, as indicated below.

The behaviour observed at the anode in the case of the electrolysis of sodium benzoate solution suggests that the badly-conducting sulphuric acid which appears, in electrolyzing that liquid, at the anode, may under certain conditions be able to stop the current. In discussing such a hypothesis we have to remember :—

(1) That the specific resistance of H_2SO_4 increases very rapidly with the degree of concentration.

(2) That the concentration of the acid at the anode during electrolysis is partially prevented (*a*) by the evolution of oxygen (as we have pointed out, *ante*, p. 164), and also (*b*) by its dilution, the rapidity of which depends on the viscosity and strength of the acid solution used.

(3) That a certain amount of oxygen forms a gaseous layer on the anode.

Bearing these points in mind, we will examine whether they are sufficient to explain our experiments.

Firstly. With low current-densities the concentrated acid will be formed in quantity too small to withstand the two causes tending to cause its dispersion.

Secondly. With greater current-densities the rate of formation of the concentrated acid will overcome the rapidity of its dilution, and the resistance of the layer of acid round the anode may increase so rapidly as to form an insulating film, before enough gas has been evolved to cause its destruction ; the gas which has been produced becoming entangled in the viscous concentrated layer, which, once formed, will not be easily removed by friction, &c.

Thirdly. With still higher current-densities, though there will be a greater tendency towards the formation of this layer immediately the circuit is made, yet it is conceivable that more gas will be produced in the same time than can be prevented from escaping, and thus destroying the non-conducting layer ; for it would be expected that the tendency of the gas to escape would increase at a greater rate than the tendency of the acid layer to prevent the escape. An *upper limit* to the current-density ought therefore to be discoverable beyond which no film can be produced. In the case of foil electrodes placed horizontally with only the lower surface exposed to the acid, we have succeeded in obtaining such an upper limit. The discovery of an upper limit makes some of our experiments of less value, for where we have stated that no film has been obtained, the non-success may be due to failure in fixing on the right limits of current-density. It also explains the peculiar jumps in the current which we have at times observed in using platinum electrodes in strong H_2SO_4. These jumps, which were of a similar kind to those which we obtained with gold electrodes, are probably due to the current-density used being near the upper limit when small causes, such as the heating of the liquid, would involve the disappearance of the film *

* We are not disposed to think that the jumps obtained with gold are due to the same cause. Gold really comes under the head of attackable electrodes, and the phenomena with it are, therefore, probably of a more complicated character than with either platinum or carbon. Palladium, in this respect, must be classed with gold, for, when used as anode in moderately strong sulphuric acid, it dissolves.

This provisional hypothesis likewise accounts for the non-formation of the film in dilute H_2SO_4* Here the rate of dilution (even if the electrolyte be made viscous by the addition of glycerine) of the concentrating layer will be more rapid, and hence a greater length of time would be required to produce a thoroughly concentrated layer. But the longer the time that elapses before this is attained, so much the greater must be the quantity of oxygen produced. Thus, just as in the case of current-densities above the upper limit in strong H_2SO_4, the formation of film will be prevented.

The less rapid increase of the specific resistance with the degree of concentration in the cases of H_3PO_4 and KHO probably explains the difficulty found in obtaining such a high degree of insulation as we have observed with H_2SO_4.

Some other aspects of transition resistance, evidenced by some experiments not included here, will be considered in a subsequent paper.

XLVI. *Note on some Additions to the Kew Magnetometer.* *By* T. E. Thorpe, *Ph.D.*, *F.R.S.*, *and* A. W. Rücker, *M.A.*, *F.R.S.*†

In making field observations with the Kew magnetometer it is important that the mirror by which the image of the sun is formed should either be in perfect adjustment, or that the errors should be known and allowed for.

The axis about which it rotates is made horizontal by means of a riding level. The plane of the mirror is made parallel to the axis by adjusting it until the image of the cross wires formed by reflexion in the mirror does not alter its position when the mirror is inverted in its bearings. The axis of the mirror is made perpendicular to the optic axis of the telescope by making the cross wires and their image coincident. In the course of the Magnetic Survey of Great Britain and Ireland, on which we have been for some time engaged, we have found such great difficulty in making these adjustments in the field, that we have for a long time practically abandoned this

* The results obtained by Christiani, we believe, may also be explained by this hypothesis.

† Read June 9, 1888.

method, and adjusted the mirror from time to time, either indoors by means of a plumb-line, or by observations on some convenient object external to the instrument in the field. We have always, when possible, made four sets of sun observations, reversing the mirror in its bearings, and taking "front" and "back" views, in which the observer looks towards the sun and stands with his back to it respectively. We have thus been able to eliminate the errors of adjustment of the mirror, and to assure ourselves that each observation was satisfactory.

This method is, however, open to some objection. When the sky is cloudy it may be impossible to see the sun for a time sufficient to take all four sets of observations. On such occasions we always pay special attention to the adjustment of the mirror, but it may happen that no object near the station is sufficiently elevated to be used for the purposes of correction. In that case it is necessary to rely on the result of a long experience, which proves that if reasonable care is taken of the instrument the mirror does not get seriously out of adjustment during a journey by road or rail extending over a day or two.

Nevertheless, there can be no doubt that the method of correcting by the image of the cross wires has the advantage that it can, theoretically at all events, be carried out at the place and time at which the observations are made.

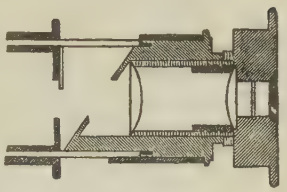
The practical drawback which led us to abandon it was the difficulty of seeing the image of the wires. In the neighbourhood of the cross wires the metal of the telescope tube is cut away, but the light thus admitted is insufficient. On a gloomy day, when the sun was only visible at rare intervals, and when, therefore, it was most important that the mirror should be in order, the necessary adjustments could not be made. Even on a bright day it was desirable to envelop the observer's head and the instrument in a dark cloth, and this was difficult and troublesome if the wind was high.

We have, therefore, lately devised some additions to the magnetometer which, although extremely simple, make it practically possible to use the cross wires for making the adjustments.

A polished platinum mirror is introduced into the telescope between the eye-piece and the cross wires, which are viewed

through a hole in its centre. The mirror is inclined at 45° to the axis of the telescope, and reflects a considerable quantity of light upon the wires. A bronzed brass tube is attached to a support which fits into the three holes which are provided to fix the magnet-box in position. This tube extends from the telescope to the mirror, and thus shuts out extraneous light. It can be packed in the ordinary magnetometer-box, and when it is in position, and the platinum mirror is directed towards the sky, or, if desirable, towards its brightest part, the image of the wires can readily be seen. If the background reflects much light, it is desirable to place a small blackened metal screen weighted with lead on the horizontal circle which carries the mirror. This can be lifted off without in any way interfering with the adjustments.

Fig. 1.



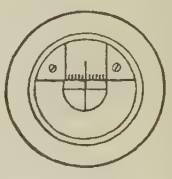
The following two examples may serve to indicate the degree of precision with which the adjustment of the mirror can be made.

Observations were taken both when the observer was looking towards and directly away from the sun. The N point on the circle is deduced from the front observations. The collimation correction is obtained by combining the front and back observations. It will be seen that the uncorrected results are quite as good as those to which the collimation correction has been applied, which proves that the mirror can be adjusted to within the limits of the error of observation on the sun.

Station.	G. M. T.	Altitude of Sun.	N point on Circle.	Collimation correction.	Corrected N point.
	h. m. s.	° ′	° ′	°	° ′
Horsham.	12 43 49	50 2·2	297 4·2	+0·3	297 4·5
(April 21,	15 15 44	34 33·7	297 3·8	−0·6	297 3·2
1888.)	17 4 0	18 12·7	297 3·6	−0·1	297 3·5
Alresford.	14 10 36	45 7·8	241 23·0	−0·1	241 22·9
(April 28, 1888.)	15 45 6	.....	241 22·5	Not determined.	

In cases where it is for any reason impossible to take the back observations, or if the sun is so frequently covered that it is advisable to observe without waiting to adjust the mirror, it is advantageous to be able to determine how much error has been introduced. For this purpose we have placed in the plane of the cross wires a fine scale engraved on ivory. The angular deviation of the mirror which produces a given displacement of the image of the cross wires on this scale can be determined, and when this is known the error of the mirror can, on any subsequent occasion, be deduced from the deviation of the image.

Fig. 2.



The following observations were made in a lofty room on an object the elevation of which was 40° :—

Scale Reading of Image of Cross Wires (x).	Reading on Circle (ρ).	$x-x_0$.	$\rho-\rho_0$.
−5·65	264° 42′·1	−5·45	6·4
−3·60	264 39·5	−3·40	3·8
−0 20	264 35·7		
+2·80	264 32·6	3·00	−3·1
+5·45	264 29·0	5·65	−6·7

All the readings are the mean of two which differed but little, and between which the axle of the mirror was inverted in its bearings. Hence if α be the angular value of a scale-division, *i. e.* the error of collimation of the mirror which corresponds to a displacement of the image through one division,

$$\rho-\rho_0=\frac{2(x-x_0)\,\alpha\sin^2 20^\circ}{\cos 40^\circ}$$

$$=0{\cdot}306\,(x-x_0)\,\alpha.$$

We thus get four values of α, viz. 3′·8, 3′·7, 3′·4, and 3′·9, the mean of which, viz. 3′·7, may be taken as correct.

To check this value, observations were made at South Kensington on the sun, and on a pinnacle of the Natural

History Museum, both when the mirror was in good and when it was in bad adjustment. It will be seen that the corrected values are in close accord.

Thus on May 9th, at $12^h\ 46^m\ 36^s$, when the altitude of the sun was $54°\ 39'{\cdot}8$, the N point on the scale was found to be $58°\ 11'{\cdot}2$. The mirror was then thrown out of adjustment, the mean reading for the image of the cross wires being $+5{\cdot}7$ div. Another observation on the sun was made at $1^h\ 13^m\ 12^s$, when the altitude was $52°\ 51'{\cdot}5$, which gave for the reading of the north point $57°\ 56'{\cdot}9$.

The correction is

$$\frac{2 \times 5{\cdot}7 \times 3{\cdot}7 \sin^2 26°26'}{\cos 52°\ 51'} = 13'{\cdot}8.$$

Hence

$$57°\ 56'{\cdot}9 + 13'{\cdot}8 = 58°\ 10'{\cdot}7,$$

which differs only by half a minute from the value obtained when the mirror was in adjustment.

In like manner the bearing of a pinnacle, as given by the mirror in adjustment, was $128°\ 40'{\cdot}8$, while, when the reading for the image of the cross wires was $+5{\cdot}7$ div., it was.

$$128°\ 40'{\cdot}2 + 0'{\cdot}8 = 128°\ 41'{\cdot}0.$$

The elevation was $15°\ 39'$, and the two results agree to $0'{\cdot}2$. It is evident from these test cases that, since the error of the mirror was far larger than that produced by travelling for a day or two, observations in the field can, by means of the scale, be corrected to within the limits of the error of experiment.

The additions to the magnetometer, which we have here described, were made for us by Messrs. Elliott, and we venture to think that they might with advantage be incorporated in standard instruments of the Kew pattern.

XLVII. *Note on Continuous-current Transformers.* *By* Professor Silvanus P. Thompson*.

It has often been proposed to distribute electric energy from central stations to local distributing stations by means of transformers, which receive small currents at high potential and transform them into large currents at low potential. When alternating currents are employed, induction-coils of appropriate construction are used as transformers. But the use of such currents is attended by two disadvantages: namely, that alternate currents cannot be used for electrochemical purposes, and that, pending the invention of a satisfactory alternate-current motor, they cannot be used for the actuating motive machinery. When continuous currents are used, the appropriate transformer may be one of two types —(1) the motor-generator, (2) the commuting-transformer.

The motor-generator in its primitive form consists of a motor to receive the incoming current, geared mechanically to a generator which produces the outgoing current. A more specialized form consists of a single machine with one field-magnet and two armatures; one to receive the primary current, the other to generate the out-going or secondary current. If the two sets of armature-windings are coiled around the same core, each set of windings being furnished with an appropriate commutator and collecting-brushes, the development has reached its extreme case, the only remaining point being the proper method of excitation of the field-magnet.

The commuting-transformer is a more complex apparatus, and has been much misunderstood. It does not necessarily involve any greater amount of sparking than any ordinary dynamo. The general principle of this species of transformer may be explained by reference to a particular type. Suppose that an armature double-wound with a primary coil to receive the incoming current, and a secondary coil to generate the outgoing current, have been provided as in the previous case, each coil having its appropriate commutator. To enable this piece of apparatus to transform the currents, it must either be

* Read June 23, 1888.

allowed to rotate in a magnetic field between the poles of a field-magnet, or else the field-magnet (and collecting-brushes) must be arranged to rotate, in the opposite sense, around it. But there is a third possible arrangement, namely to rotate around it the magnetic polarity while itself remains fixed. This may be done either by rotating the brushes which bring in the primary current, the magnetic circuit being completed by a mass of iron external to the ring, or by rotating also the polarity of a fixed field-magnet constructed specially for this purpose. An external fixed ring of Gramme or Pacinotti pattern, provided with a commutator, will answer for this purpose, the current being supplied by a pair of brushes which is rotated. In such a machine obviously all the parts are stationary save the revolving brushes, which must be driven by some mechanical device. Various modifications of this idea have from time to time been suggested.

The theory of alternate current-transformers has been investigated by various authorities. It was first shown by Maxwell that where there is mutual induction between two circuits, the effect upon the secondary circuit of the presence of the primary circuit is threefold :—(*a*) to transform in a certain ratio the electromotive force ; (*b*) to add to the resistance of the secondary circuit an apparent resistance equal to that of the primary multiplied by the square of the same ratio; (*c*) to deduct from the coefficient of self-induction of the secondary circuit a quantity equal to the coefficient of self-induction of the primary circuit multiplied by the square of the same ratio. The ratio in question was found to be the quantity

$$\frac{2\pi n\mathrm{M}}{\sqrt{4\pi^2 n^2 \mathrm{L}_1{}^2 + \mathrm{R}_1{}^2}} ;$$

where M is the coefficient of mutual induction, n the number of alternations per second, L_1 and R_1 the coefficient of self-induction and the resistance respectively of the primary circuit. In a communication made last year to this Society I showed how, assuming the proper conditions of good construction to have been observed, this ratio was equal to the ratio of the number of secondary windings to the number of primary windings in the transformer ; which ratio is known as the "coefficient of transformation."

The object of the present paper is to show that in continuous current-transformers effects of the same kind exist. The investigation is of an elementary character, secondary reactions being assumed to be negligibly small.

Consider a motor-generator, with double-wound armature of ring or drum type, arranged to rotate between the poles of a common fixed field-magnet. The magnetism of the latter may be considered for present purpose constant: the effect of variation in the magnetization will be afterwards considered. Let the number of armature-conductors of the primary or motor part, as counted all round the periphery, be called C_1, and that of the secondary part be called C_2. The ratio of C_2 to C_1 we may call *the coefficient of transformation*, and we shall use k as the symbol of this ratio.

Now let i_1, r_1, and E_1 stand respectively for the current, the resistance, and the induced electromotive force in the coils of the primary armature, and i_2, r_2, E_2 for the corresponding quantities for the coils of the secondary armature. Write N for the whole number of magnetic lines passing through the armature-core. Also write e_1 and e_2 for the respective differences of potential at the terminals of the primary and secondary parts.

We shall then have

$$E_1 = nC_1N \,.\, 10^{-8},$$
$$E_2 = nC_2N \,.\, 10^{-8};$$

whence

$$E_2/E_1 = C_2/C_1 = k,$$

whatever the values of speed and field may be. Further,

$$E_1 = e_1 - r_1 i_1,$$
$$E_2 = e_2 + r_2 i_2;$$

whence

$$e_2 = ke_1 - r_2 i_2 - kr_1 i_1.$$

Now assume that the work wasted in the armature in mechanical and magnetic friction, and in producing eddy-currents, is negligibly small compared with the work done in driving the generator part. This is, in fact, merely assuming that the machine is properly designed and constructed; for in such machines, there being no driving-belt, the only forces except gravity are centrally balanced, and mechanical friction

at the bearings is a minimum ; and further, if the iron core is of proper quality and quantity, and properly laminated and insulated, the losses due to hysteresis and eddy-currents are very small*. We shall then have the work $E_1 i_1$ done by the primary current (in unit time) equal to the work $E_2 i_2$ done on the secondary current. Consequently $i_1 = k i_2$. Inserting this value, we at once get

$$e_2 = k e_1 - (r_2 + k^2 r_1) i_2.$$

This shows that everything goes on in the secondary circuit as though the induced electromotive force was transformed from the difference of potentials at the terminals of the primary circuit in proportion to the respective numbers of windings on the armature, and as though there were then added to the real internal resistance of the secondary circuit a resistance equal to that of the primary winding multiplied by the square of the coefficient of transformation. If there are equal weights of copper in the primary and secondary windings, the actual resistances of the two windings will be proportional to the squares of the numbers of turns : hence the effect of multiplying r_1 by k^2 is to make it equal to r_2 ; in other words, the added virtual resistance is equal to the real internal resistance.

With respect to self-induction and its effects in such machines, it may be remembered that, in an ordinary single-wound dynamo, the effect of self-induction is to add to the armature a spurious resistance, owing to the successive stoppage and restarting twice in every revolution of the current in each section. Now if matters were so arranged in the double-wound machine that commutation of the current in any one section of the primary should occur exactly at the same instant as commutation of the current in that section of the secondary wire which was wound over the same part of the common core, it is clear that, as the currents in the primary and secondary circulate around the core in opposite senses, the stopping of the current in the one would tend to stop the (inverse) current in the other, and the starting again of the current in the one would tend to start the inverse

* If F be the waste work done against mechanical and magnetic friction, the formula becomes

$$e_2 = k e_1 - i_2 (r_2 + k^2 r_1 + F/i_2^2).$$

current in the other. In other words, the mutual induction between the two sections would tend to counteract in both the effects of self-induction. In practice it is impossible to fully realize this neutralizing effect; but that it is very nearly realized is evidenced by the almost complete absence of sparking in such machines.

In the above argument it has been assumed that the magnetism of the field-magnet was constant in amount; but incidentally it was noticed that the expressions were independent of the magnetic field. The more powerful this is, the slower need the armature run to generate the respective electromotive forces. Assuming that the transformer is supplied at constant potential at its primary terminals, and that the internal resistance of the secondary winding is small, it will be self-regulating, giving a constant potential at its secondary terminals quite irrespective of the variations of its speed with the load.

In yet one other respect does the action of the motor-generator resemble the alternating transformer: when supplied at constant potential it is almost exactly self-regulating in respect of its automatic action in adjusting the amount of the inflowing primary current, in proportion to the outflowing secondary current. When the secondary circuit is entirely opened, the motor part runs just so fast that the back electromotive force E_1 in the primary part increases and dams back the primary current; only just so much flowing through as will suffice to drive the machine against the reactive forces of mechanical and magnetic friction.

Precisely similar relations to those traced out for motor-generators hold good in the commuting-transformers. The reactions between the primary and secondary windings go on exactly the same, whether the successive displacement in the polarity of the magnetization through the common core of the armature be accomplished by mechanically rotating it, or by electrically shifting the polarity of the surrounding field-magnet in a rotatory fashion. With equal weights of copper in the primary and secondary coils of the armature part, the effect of mutual induction will here also be approximately to double the internal resistance and to neutralize the self-induction of the secondary winding.

XLVIII. *On the Existence of an Undulatory Movement accompanying the Electric Spark.* *By* Ernest H. Cook, *D.Sc.* (*Lond.*), *F.I.C.*, *Merchant Venturers' School, Bristol**.

[Plate XI.]

1. If a powdered substance be scattered over a smooth plate, and the plate held near a pair of terminals between which an electric spark is passing, the powder will arrange itself in a more or less regular series of concentric circles. The common centre of these circles (when the spark is small) appears to be a point directly under that halfway between the terminals. The general appearance presented by these curves will be apparent by a glance at the figures in the Plate which accompanies this paper. These are approximately of the same size as the original. It will be noticed that the figures roughly divide themselves into two classes—(1) those with a clear space in the middle, and (2) those with a circular space, within which the powder is apparently unaffected.

The first class are obtained by holding the plate near to the terminals, the distance varying with the energy of the spark. The cleared space is irregularly elliptical, with its major axis at right angles to the direction of the spark, and the area of the space increases as the intensity of the spark increases. The second class are formed when the distance between the spark and plate is increased until the elliptical space ceases to make its appearance.

2. *Mode of Obtaining the Curves.*—The most convenient arrangement and the one which gives the best results is as follows:—An induction-coil has each of its terminals connected with a Leyden jar, and with one of the handles of a universal discharger. The plate with the powder scattered over it from a sieve is held under the points at a distance which can be varied at pleasure. The distance between the terminals, and therefore the length of the spark, can also be easily adjusted. On connecting the coil to the battery a

* Read June 23, 1888.

The paper was illustrated by a series of photographs: from two of these the figures in the Plate have been engraved.

succession of sparks of condensed electricity is obtained, and the powders will be seen to arrange themselves in the manner described. The first spark causes a distinct effect, but a continuance is necessary to bring out the regularity of the curves.

Should it be required to fix the powders in the positions which they have taken up, it is easily done by coating the plate beforehand with a thin layer of gum, and after the experiment breathing on it.

3. *Effect of Plate.*—When the figures were first obtained it was surmised that they might be caused by the distribution of the electricity over the plate ; that they were in fact modified Lichtenberg's figures. Experiments were therefore made with plates of various substances in different states as regards their surfaces; for example, whether polished or dull, electrified or unelectrified. The following materials have been examined:—glass ; resinous cake of electrophorus (a mixture of shell-lac, resin, and Venice turpentine) ; ebonite ; paper (glazed and unglazed) ; brass (lacquered and unlacquered) ; zinc ; iron, tinned ditto, galvanized ditto; wood; paraffin; cardboard ; and glazed and unglazed earthenware. Except that the rougher surfaces retard and prevent the regularity of the curves, no difference whatever could be observed as due to the substance or condition of the surface.

A piece of plate-glass or polished sheet of metal answers admirably for these experiments. The fact that the production of the curves is independent of the electrical state of the support (and therefore of the powder) justifies the statement that they are not caused by any peculiarity of electrical distribution.

4. *Effect of Battery Power, Coil, and Condensation.*—Experiments were made with the view of finding if variations in the number of cells, in the coil, and in the capacity of the condensers used, caused any alteration in the shape or frequency of the lines in which the powders arranged themselves. Other conditions remaining constant, the battery power employed to drive the coil was changed from ten pint bichromates to one. In no case could any difference be observed in the resulting figures produced. Afterwards the current was still further reduced until it was just sufficient

to drive the coil, but so long as this was accomplished the figures remained unaffected.

Several coils were used in the course of the earlier experiments, but finally the work was confined to two. One of these was a very fine instrument by Ruhmkorff, kindly lent to me for the purpose of these experiments by Mr. Francis J. Fry, late High Sheriff of Bristol. It contains a secondary coil, formed of twenty-four miles of wire, is fitted with both spring and mercury interrupters, and with one bichromate (carbons $7'' \times 3\frac{1}{2}''$), gives a regular succession of sparks six inches long. The second was a smaller instrument, by Paterson of London, fitted with a condenser of 100 sheets of 12″ by 5″, and capable of giving a small spark of about $1\frac{1}{2}$ inch long. When coupled with the Leyden jars, of course, the length of spark was much diminished. In no case with either coil was a longer spark employed than ·75 inch. No change in the appearance, regularity, or shape of the figures was caused by replacing one coil by another.

The effect of a difference in condensing-power was tried by interposing more jars. Except that the vigour of the spark caused a larger area of cleared space, no alteration could be observed. This is, of course, confirmed by the fact of the different coils, possessing condensers of different areas, giving identical results.

5. *Influence of Contact-Breaker.*—It might be supposed, as was done by Grove in reference to the stratifications in partial vacuo, that the intermittent character of the currents flowing in the secondary wire caused by the interruptions in the primary-coil by the contact-breaker would have some influence in producing or regulating the curves. This, however, is not the case. The shapes did not alter no matter what coil was employed, and when the mercury-break on the large coil was used in place of the spring, no alteration in the resulting curves was produced. Moreover the curves can be obtained without the use of a coil with its necessary contact-breaker at all. For this purpose it is only necessary to connect each electrode of a Wimshurst machine to one or two Leyden jars, and to allow the highly condensed spark thus obtained to act upon the powder. In fact I have been able to produce the curves in this way without employing any jars at all. With

the machine, however, they are far inferior in regularity to those produced by the use of the coil. With a 17-inch plate the best results have been obtained with jars having a total area of foil of about 1500 square inches, a spark of about 3″ long, and the powder 6″ below spark.

6. *Nature of Electrodes.*—Varying the material forming the points between which the sparks were taken made no difference in the resulting shapes. Thus the same effects are produced by using brass, iron, or carbon points.

7. *Influence of the Powdered Substance.*—Soon after the first results were obtained and upon trying different substances, it became evident that, although accidental irregularities occurred, yet, upon the whole, the curves were remarkably regular. It was also very soon noticed that the frequency with which they followed each other altered with an alteration of the substance of which they were composed. This induced a desire to compare by measurement the distances between each successive curve. A large number of different powders were examined, and the number of lines in a certain distance counted. Several determinations were made and the mean number taken. Although every care was taken to make these measurements as accurately as possible and to avoid sources of error, yet, from the difficulties peculiar to the case, I do not wish to pledge the absolute accuracy of the numbers, but put them forward as approximate only. It first became necessary to ascertain if the fineness of the powder affected the number of lines in a certain length. This was found not to be the case. Provided the degree of fineness was such as to admit of the production of the lines with such an amount of definiteness as sufficed for their measurement, the number of lines was found to be unaltered. The following tabular statement gives the results obtained. The actual experiment was to count the number in a quarter of an inch. These have been multiplied by 4, hence the regularity of the diminution of the numbers given in the first column:—

No. of lines in 1 inch.	Substances examined.
88.	Silica (powdered sand).
80.	Magnesia alba.
68.	Chromic oxide.
64.	Antimony sulphide; baric peroxide; fluor spar; cupric oxide; red lead; lead acetate; lead oxide; antimony; sulphur; potassium hydrogen tartrate.
60.	Borax; cobaltic oxide; starch; zinc carbonate.
56.	Binoxide of manganese; baric carbonate; tricalcic phosphate; ferrous sulphide; lead chromate; mercuric oxide; binoxide of tin; nickel monoxide; lead carbonate; calcic oxide.
52.	Sodium hydrogen carbonate; potassic sulphate; potassic carbonate; mercurous chloride; carbon; calcic hydrate.
48.	Tannin; salicylic acid; rochelle salt; ammonic sulphate; baric nitrate; copper sulphate; oxalic acid; sodic chloride; succinic acid; Epsom salts.
44.	Alum.
40.	Chalk.
The figures were so indefinite as to permit counting.	Iron filings; baric chloride; baric sulphate; benzoic acid; strontium chloride; bismuth nitrate; cadmium nitrate; microcosmic salt; potassium chloride; potassium bromide; ammonium chloride; ferrous sulphate; ammonium nitrate; pyrogallol.

8. *Effect of Mixture.*—While engaged in repeating the experiments, in order to confirm the numbers, it was found that a particular sample of calcic oxide gave 48 lines to the inch instead of 56, as given in the table. Upon examining the sample it was found, however, to be an old one, and to be partially converted into carbonate. It was thus a mixture of oxide and carbonate. This led to the investigation of other mixtures. It was thus proved that the number given by a mixture of two substances was intermediate between those of its constituents. The following were examined, no particular care being taken to mix in definite proportions, but the substances simply ground up together in a mortar :—

Mixture.	Nos. due to each constituent.	No. obtained.		
		Exp. 1.	2.	3.
Calcic oxide	56	48	50	48
Calcic carbonate	40			
Magnesia alba	80	60	64	56
Calcic carbonate	40			
Cobaltic oxide	60	64	64	66
Chromic oxide	68			
Cobaltic oxide	60	68	64	68
Magnesia alba	80			

9. *Effect on Liquids.*—In order to test if the effect could be produced on the surfaces of liquids the following experiments were made:—In place of a glass plate with the powder scattered over it, there was held under the spark a shallow vessel (an ordinary porcelain evaporating dish answers very well) containing the liquid. So long as the surface was looked directly down upon, no effect could be observed; but when regarded obliquely, minute ripples were seen to be produced upon the surface. No attempt was made to measure these, but they were judged to be of about the same size as those of the powders, that is, between the limits of 88 and 40 to the inch. The following were the liquids tested in this way:—water, mercury, alcohol, ether, glycerin, and benzol.

10. *Experiments with Wimshurst Machine.*—It has already been stated that the curves obtained by the aid of the machine are much inferior in regularity to those given by the induction-coil; in fact, without care they cannot be produced at all. But there are some other peculiarities which deserve notice. Thus, while with every coil used and with varying battery-power it was found that magnesia alba gave 80 lines to the inch, when the machine was used the number varied in different parts of the figure from 56 to 64. There was no particular mode of variation, that is, no crowding together at a special place, &c. This irregularity in the numbers is not, however, a general thing; for in other cases tried, the numbers did not vary among themselves and agreed with those obtained with the coils.

The common centre of the circles, instead of being, as with

the coil, halfway between the terminals, seemed to be a little nearer the positive electrode than the negative. Other experiments are, however, necessary before this can be regarded as established.

In experimenting with this machine it is necessary to avoid placing the plate too near the terminals, otherwise the powder becomes electrified, and the plate also, and the resulting figures are combinations of those showing the distribution of the electricity upon the plate, and the undulatory effect discussed in this paper.

Most of the figures obtained with the machine were caused by the spark passing between knobs. They are imperfect at the sides, in consequence of the undulatory effect being prevented from making itself felt in those directions by the solid body of the knob coming between. Thus the portion of the circles shown are at right angles to the direction of the spark. The figure can of course be obtained from sparks taken between points, but it is more difficult. It was particularly noticed in the course of these and some other experiments that, whilst substituting a knob for a point in a Wimshurst or other machine increased the length of spark obtainable, it was just the opposite with a coil; for here the spark is considerably reduced if taken between *two* knobs. The longest spark with a coil is obtained either between two points, or between one point and one knob or plate.

It was also noticed that under the positive electrode the powder was scattered so as to cause a space. This is sometimes, but not always, the case under the negative.

11. *Production of the Cleared Space.*—It will be observed that the more or less elliptical space in the middle of the figures is not present in all. It is only produced when the plate is held close up to the terminals and when the vigour of the spark is considerable. At a first glance at a figure containing the clear space, it appears that the lines are crowded together at the ends of the major axis of the ellipse. Closer examination and careful measurement will show, however, that this is not the case, for the number of lines per unit of length is the same whether measured at the ends of the major or of the minor axis. In fact the appearance is just that of concentric circles, formed of the powder, with the material

composing the smaller circles swept up so as to form the irregular ellipse.

From this fact, and also that the circles can be produced without any clearing of the powder, I am led to conclude that the production of the circles is due to *an entirely different cause* to that producing the space, but that both are necessary accompaniments of the disruptive discharge.

12. *Discussion of Results.*—When these figures were first obtained it was imagined that they were due to the sound which accompanied the spark, and in fact gave a graphical representation of the sound-waves. This view was to some extent confirmed by finding that the same substance gave the same number of waves in the same space. If this be so, however, then there ought to be no difference in the numbers obtained with different powders; for the sound of the spark produced by a coil is remarkably constant, and, if such a term can be rightly applied to it, it is of unvarying pitch. This view, however, is also disproved by the measurements; for if it be taken that the lines show the phases of the undulatory movement, then the longest distance between similar phases is that given by powdered chalk, viz. $\frac{1}{40}$ of an inch. But the upper limit of vibration producing a sound-wave may be taken as equal to 40,000 per second, giving a length for the wave of as nearly as possible one third of an inch, a distance thirteen times greater than the longest given by these experiments. It is therefore evident that the vibrations producing these curves and those producing the sound of the spark are not identical.

From the fact that the number given by a mixture is intermediate between those of its constituents, we should be led to conclude, since the density of a mixture follows the same law, that therefore this is the factor which regulates the number given by any particular substance. If this be the case, then the powders should arrange themselves in a series, with those of the highest density at the top and those of the lowest at the bottom. A glance at the tables of results will, however, show that no such order is observed. Thus we have silica giving a higher number (88) than the heavy oxides of lead (64); magnesia alba, a substance of very low specific gravity, appearing high up in the list; and tannin, also of low specific

gravity, on the other hand, appearing low down. What conditions, if any, regulate the number of these lines I have hitherto been unable to determine. Before any generalization can be made it is necessary to examine a very much larger number of substances, and experiments are being conducted with this purpose. At present, indeed, I am not disposed to attach much importance to the absolute length of any one of these undulations, but rather to the great similarity of the measurements as a whole. For although it is likely that errors may occur in some of the individual members, it is hardly possible that the whole are erroneous. It will therefore follow that undulations of a length of about one sixty-fourth of an inch (taking the mean measurement) accompany the disruptive discharge.

The photographs from which the figures in the Plate are copied were taken for me by Mr. Dunscombe, of Bristol, and were printed from the negatives without the latter being touched in any way.

Note, June 9, 1888.—Since the above was written, I have been informed by Prof. Rücker that he has an apparatus in his possession, made by the late Dr. Guthrie, which gives somewhat similar results. This was copied from one exhibited at the Loan Exhibition of Scientific Apparatus in 1879. It consists of an elliptical dish with vertical walls. Sand is scattered over the bottom, a glass plate placed over the top, and a series of electric sparks produced at one focus of the ellipse. The sand will then be found to arrange itself in a series of circular curves around the other focus. The curves thus produced bear a striking resemblance to those exhibited in the Plate accompanying this paper, and are of course due to the same cause.

XLIX. *On a new Form of Lantern.*

By W. Lant Carpenter, *B.Sc.*

Mr. W. Lant Carpenter exhibited (June 9, 1888) a new form of Lantern, recently constructed by Mr. Hughes, of Dalston. The mahogany body is hexagonal, and each of the three front

sides is provided with condensers and projecting arrangements. The back opens to give access to the radiant, which in this case is a Brockie-Pell Arc-Lamp ; but, if necessary, a lime-light can be readily substituted. The lamp is fixed to the base-board, and the body can be rotated through 60° on either side of the central position, thus allowing any of the three nozzles to be directed towards the screen. The three sets of condensers are placed so that their axes intersect at a point about which the radiant is placed. The centre nozzle is fitted as a lantern-microscope, with alum cell and various sets of condensing-lens and objectives, and a space in front of the main condensers is provided for polarizing-apparatus. The focusing arrangement consists of a skew rack and pinion and a fine screw-adjustment ; and the whole microscope can be easily removed and a table-polariscope substituted. The right-hand nozzle is arranged for the projection of ordinary lantern-slides, and the left-hand one is provided with an adjustable slit for spectrum work. A small table sliding on rails serves to carry the prisms, and the same rails support projecting lenses.

Prof. S. P. Thompson congratulated Mr. Lant Carpenter on his selection of the Brockie-Pell lamp as the radiant ; for, in addition to its being a focusing-lamp, it is unique in the fact that it works satisfactorily on either constant-current or constant-potential circuits.

INDEX.

A.

Page

Abercromby, Hon. Ralph, observations on the height, length, and velocity of ocean waves 150
Addenbrooke, G. L., on a compact form of reflecting-galvanometer, lamp, and scale 263
Alternating electric currents, on a geometrical determination of the conditions of maximum efficiency in the case of the transmission of power by 85
Analogies of influence-machines and dynamos 260
Analogy between solutions and gases, the function of osmotic pressure in the 307
Aubel, Edmond van, an experimental study on the influence of magnetism and temperature on the electrical resistance of bismuth and its alloys with lead and tin..... 124
Ayrton, W. E., and Perry, John, on beams fixed at the ends 56
——— ———, the efficiency of incandescent lamps with direct and alternating currents..... 208
——— ———, note on the governing of electromotors..... 296
——— ———, the magnetic circuit of dynamo machines..... 220

B.

Beams fixed at the ends, note on 56
Bidwell, Shelford, on the electrical resistance of vertically-suspended wires 3
Bismuth, the effect of magnetization on the thermoelectrical and other physical properties of 139
Blakesley, Thomas H., on a geometrical determination of the conditions of maximum efficiency in the case of the transmission of power by means of alternating electric currents..... 85
———, on a method of determining the difference between the phase of two harmonic currents of electricity having the same period. 165
———, on magnetic lag 286

Page
Bosanquet, R. H. M., note on magnetization 19
——, on a form of polariscope for researches on the polarization of the sky 260
——, on the production of sudden changes in the torsion of a wire by change of temperature 49
——, on the use of the term "resistance" in the description of physical phenomena 201
Boys, C. V., on the production, properties, and some suggested uses of the finest threads 8
——, experiments with soap-bubbles 189
—— and Rücker, A. W., on the optical demonstration of electrical stress 263
Burton, C. V., on electromotive forces of contact 274

C.

Carpenter, W. L., on a new form of lantern 379
Change of temperature in twisting or untwisting wires which have suffered permanent torsion, the effect of 67
Changes in the torsion of a wire by change of temperature, on the production of sudden 49
Chattock, A. P., on a magnetic potentiometer 23
Coefficient of self-induction, on a modification of a method of Maxwell's for measuring the 26
Coefficients of induction, the variation of the 235
Coil of a transformer, on the measurement of the power supplied to the primary 215
Compact form of reflecting-galvanometer, lamp, and scale 263
Comparing capacities, note on 60
Continuous-current transformers, note on 366
Cook, E. H., on the existence of an undulatory movement accompanying the electric spark 371
Copper sphere and of copper wire helices, on the rotation of, when freely suspended in a magnetic field 262

D.

Dale, T. Pelham, on the numerical relation between the index of refraction and the wave-length within a refractive medium, and on the limits of refraction 167
Demonstration of electrical stress, on the optical 263
Description of physical phenomena, on the use of the term "resistance" in the 201
Determination of the conditions of maximum efficiency in the case of the transmission of power by means of alternating electric currents 85
Determining the difference between the phase of two harmonic currents of electricity having the same period, on a method of. 165

Page
Discriminating real from accidental coincidences between the lines of different spectra, on a method of 94
Dissociation, on evaporation and 33
Dynamo machines, the magnetic circuit of 220
Dynamos, on the analogies of influence-machines and 260

E.

Effect of change of temperature in twisting or untwisting wires which have suffered permanent torsion 67
—— of magnetization on the thermo-electrical and other physical properties of bismuth 139
—— on raising iron when under temporary stress or permanent strain to a bright-red heat 71
—— produced on the thermoelectrical properties of iron when under stress or strain, by raising the temperature to bright red 100
Efficiency of incandescent lamps with direct and alternating currents 208
Electric spark, on the existence of an undulatory movement accompanying the 371
Electrical resistance of bismuth and its alloys with lead and tin, an experimental study on the influence of magnetism and temperature on the 124
—— resistance of vertically-suspended wires, on the..... 3
—— stress, on the optical demonstration of 263
Electrolysis, experiments on 157
Electromotive forces of contact..... 274
Electromotors, note on the governing of 296
Evaporation and dissociation..... 33
Existence of an undulatory movement accompanying the electric spark 371
Experiment for determining the velocity of sound..... 259
Experiments on electrolysis 157, 335
—— with soap-bubbles 189
Experimental study on the influence of magnetism and temperature on the electrical resistance of bismuth and its alloys with lead and tin 124

F.

Factor of safety in the materials for lightning-rods, on the price of the..... 122
Finest threads, on the production, properties, and some suggested uses of the 8
Forces of contact, on electromotive 274
Form of polariscope for researches on the polarization of the sky.... 260
Formulæ of Bernoulli and of Haecker for the lifting-power of magnets 304
Function of osmotic pressure in the analogy between solutions and gases 307

G.

Page
Gee, W. W. H., and Holden, H., experiments on electrolysis .. 157, 335
Geometrical determination of the conditions of maximum efficiency in the case of the transmission of power by means of alternating electric currents 85
Governing of electromotors, note on the 296

H.

Harmonic currents of electricity having the same period, on a method of determining the difference between the phase of two 165
Height of ocean waves, observations on the..... 150
Hoff, J. van't, the function of osmotic pressure in the analogy between solutions and gases 307
Holden, H., and Gee, W. W. H., experiments on electrolysis .. 157, 335

I.

Incandescent lamps with direct and alternating currents, the efficiency of 208
Index of refraction and the wave-length within a refractive medium, numerical relation between the..... 167
Induction, the variation of the coefficients of 235
—— of two coils, note on Prof. Carey Foster's method of measuring the mutual 1
Influence of magnetism and temperature on the electrical resistance of bismuth and its alloys with lead and tin, an experimental study on the..... 124
—— machines and dynamos, on the analogies of 260
Iron, the recalescence of 107
—— when under stress or strain, by raising the temperature to bright red, the effect produced on the thermoelectrical properties of 100
—— when under temporary stress, or permanent strain, remarkable effect on raising to a bright-red heat 71

K.

Kew magnetometer, note on some additions to the 361

L.

Lamp, and scale, on a compact form of reflecting-galvanometer, .. 263
Lamps with direct and alternating-currents, the efficiency of incandescent 208
Lantern, on a new form of 379
Lecture experiment for determining the velocity of sound 259

Page
Lifting-power of magnets, on the formulæ of Bernoulli and of Haecker for the 304
Lightning-rods, on the price of the factor of safety in the materials for 122
Limit of refraction, on the 167
Lines of different spectra, on a method of discriminating real from accidental coincidences between the 94
Loss of the magnetic properties of iron and nickel at certain temperatures, a theory concerning the sudden 265
Love, E. F. J., on a method of discriminating real from accidental coincidences between the lines of different spectra 94

M.

Madan, H. G., on the optical properties of phenylthio-carbimide 262
Magnetic circuit of dynamo-machines 220
—— lag 286
—— potentiometer, on a 23
—— properties, the temperature at which nickel begins to lose suddenly its 181
—— properties of iron and nickel at certain temperatures, a theory concerning the sudden loss of the 265
Magnetism and temperature, influence of, on the electrical resistance of bismuth and its alloys with lead and tin 124
Magnetization, note on 19
——, the effect of, on the thermoelectrical and other physical properties of bismuth 139
Magnetometer, note on some additions to the Kew 391
Magnets, on the formulæ of Bernoulli and of Haecker for the lifting-power of 304
Materials for lightning-rods, on the price of the factor of safety in the 122
Measurement of the power supplied to the primary coil of a transformer, on the 215
Method of determining the difference between the phase of two harmonic currents of electricity having the same period 165
—— of discriminating real from accidental coincidences between the lines of different spectra 94
—— of measuring the mutual induction of two coils, note on Prof. Carey Foster's 1
Modification of a method of Maxwell's for measuring the coefficient of self-induction 26
Modified water-dropping influence-machine, on a 137

N.

New form of lantern 379
Nickel begins to lose suddenly its magnetic properties, the temperature at which 181

Page
Note on beams fixed at the ends 56
—— on comparing capacities 60
—— on continuous-current transformers..... 366
—— on magnetization 19
—— on Prof. Carey Foster's method of measuring the mutual induction of two coils..... 1
—— on the governing of electromotors 296
—— on some additions to the Kew magnetometer 361
Numerical relation between the index of refraction and the wavelength within a refractive medium, and on the limits of refraction 167

O.

Ocean waves, observations on the height, length, and velocity of .. 150
Optical demonstration of electrical stress..... 263
—— properties of phenylthio-carbimide, on the 262
Osmotic pressure, function of, in the analogy between solutions and gases 307

P.

Perry, John, and Ayrton, W. E., on beams fixed at the ends 56
——, ——, note on the governing of electromotors 296
——, ——, the efficiency of incandescent lamps with direct and alternating currents..... 208
——, ——, the magnetic circuit of dynamo machines 220
Phenylthio-carbimide, on the optical properties of..... 262
Physical phenomena, on the use of the term "resistance" in the description of 201
—— properties of bismuth, the effect of magnetization on the thermo-electrical and other..... 139
Polariscope for researches on the polarization of the sky 260
Potentiometer, on a magnetic 23
Price of the factor of safety in the materials for lightning-rods 122
Primary coil of a transformer, on the measurement of the power supplied to the 215
Production, properties, and some suggested uses of the finest threads, on the 8
—— of sudden changes in the torsion of a wire by a change of temperature 49
Properties of iron and nickel at certain temperatures, a theory concerning the sudden loss of the magnetic 265

R.

Ramsay, William, and Young, Sydney, on evaporation and dissociation 33
Recalescence of iron 107
Reflecting-galvanometer, lamp, and scale, on a compact form of.... 263

Page
Remarkable effect on raising iron when under temporary stress or permanent strain to a bright-red heat 71
Researches on the polarization of the sky, on a form of polariscope for 260
Resistance of vertically suspended wires, on the electrical 3
Rimington, E. C., note on comparing capacities 60
——, on a modification of a method of Maxwell's for measuring the coefficient of self-induction 26
——, on the measurement of the power supplied to the primary coil of a transformer 215
Rotation of a copper sphere and of copper wire helices when freely suspended in a magnetic field 262
Rücker, A. W., on a lecture experiment for determining the velocity of sound 259
——, and Boys, C. V., on the optical demonstration of electrical stress 263
——, and Thorpe, T. E., note on some additions to the Kew magnetometer 361

S.

Self-induction, on a modification of a method of Maxwell's for measuring the coefficient of 26
Sequences of reversals, on 19
Shettle, R. C., on the rotation of a copper sphere and of copper wire helices when freely suspended in a magnetic field 262
Sky, on a form of polariscope for researches on the polarization of the 260
Soap-bubbles, experiments with 189
Solutions and gases, the function of osmotic pressure in the analogy between 307
Sound, on a lecture experiment for determining the velocity of 259
Study on the influence of magnetism and temperature on the electrical resistance of bismuth and its alloys with lead and tin, an experimental 124
Sudden changes in the torsion of a wire by change of temperature, on the production of 49
—— loss of the magnetic properties of iron and nickel at certain temperatures, a theory concerning the 265
Sumpner, W. E., on the variation of the coefficients of induction .. 235
Swinburne, James, note on Prof. Carey Foster's method of measuring the mutual induction of two coils 1

T.

Temperature at which nickel begins to lose suddenly its magnetic properties 181
—— in twisting or untwisting wires which have suffered permanent torsion, the effect of change of 67

Page
Theory concerning the sudden loss of the magnetic properties of iron and nickel at certain temperatures 265
Thermoelectric properties of iron when under stress or strain by raising the temperature to bright red, the effect produced on the 100
Thermoelectrical and other physical properties of bismuth, the effect of magnetization on the 139
Thompson, Silvanus P., note on continuous-current transformers.... 366
——, on a modified water-dropping influence-machine 137
——, on the analogies of influence-machines and dynamos 260
——, on the formulæ of Bernoulli and of Haecker for the lifting-power of magnets 304
——, on the price of the factor of safety in the materials for lightning-rods 122
Thorpe, T. E., and Rücker, A. W., note on some additions to the Kew magnetometer 361
Threads, on the production, properties, and some suggested uses of the finest 8
Tomlinson, Herbert, on a theory concerning the sudden loss of the magnetic properties of iron and nickel at certain temperatures.. 265
——, on the effect produced on the thermoelectrical properties of iron when under stress or strain by raising the temperature to bright-red..... 100
——, on the effect of change of temperature in twisting or untwisting wires which have suffered permanent torsion 67
——, the effect of magnetization on the thermoelectrical and other physical properties of bismuth 139
——, on the remarkable effect on raising iron when under temporary stress or permanent strain to a bright-red heat 71
——, on the recalescence of iron 107
——, on the temperature at which nickel begins to lose suddenly its magnetic properties..... 181
Torsion of a wire by change of temperature, on the production of sudden changes in the 49
Transmission of power by means of alternating electric currents, on a geometrical determination of the conditions of maximum efficiency in the case of the..... 85

U.

Undulatory movement accompanying the electric spark, on the existence of an 371
Use of the term "resistance" in the description of physical phenomena..... 201
Uses of the finest threads, on the production, properties, and some suggested 8

V.

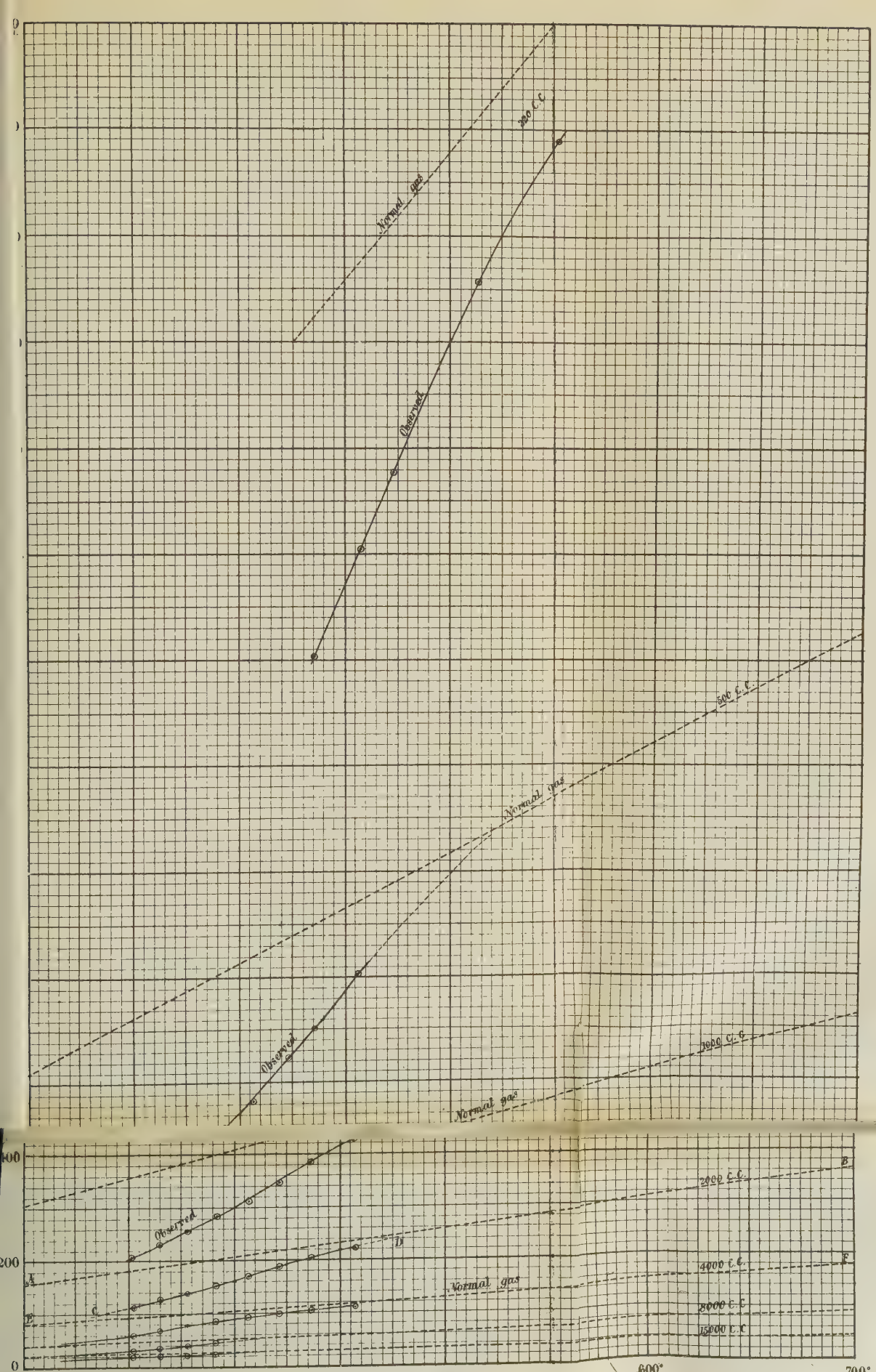
Page
Variation of the coefficients of induction, the..... 235
Vertically-suspended wires, on the electrical resistance of..... 3
Velocity of ocean waves, observations on the 150
—— of sound, on a lecture experiment for determining the..... 259

W.

Water-dropping influence-machine, on a modified..... 137
Waves, observations on the height, length, and velocity of ocean .. 150
Wire, on the production of sudden changes in the torsion of a, by change of temperature 49
Wires, on the electrical resistance of vertically-suspended 3
—— which have suffered permanent torsion, the effect of change of temperature in twisting or untwisting..... 67

Y.

Young, Sydney, and Ramsay, William, on evaporation and dissociation 33



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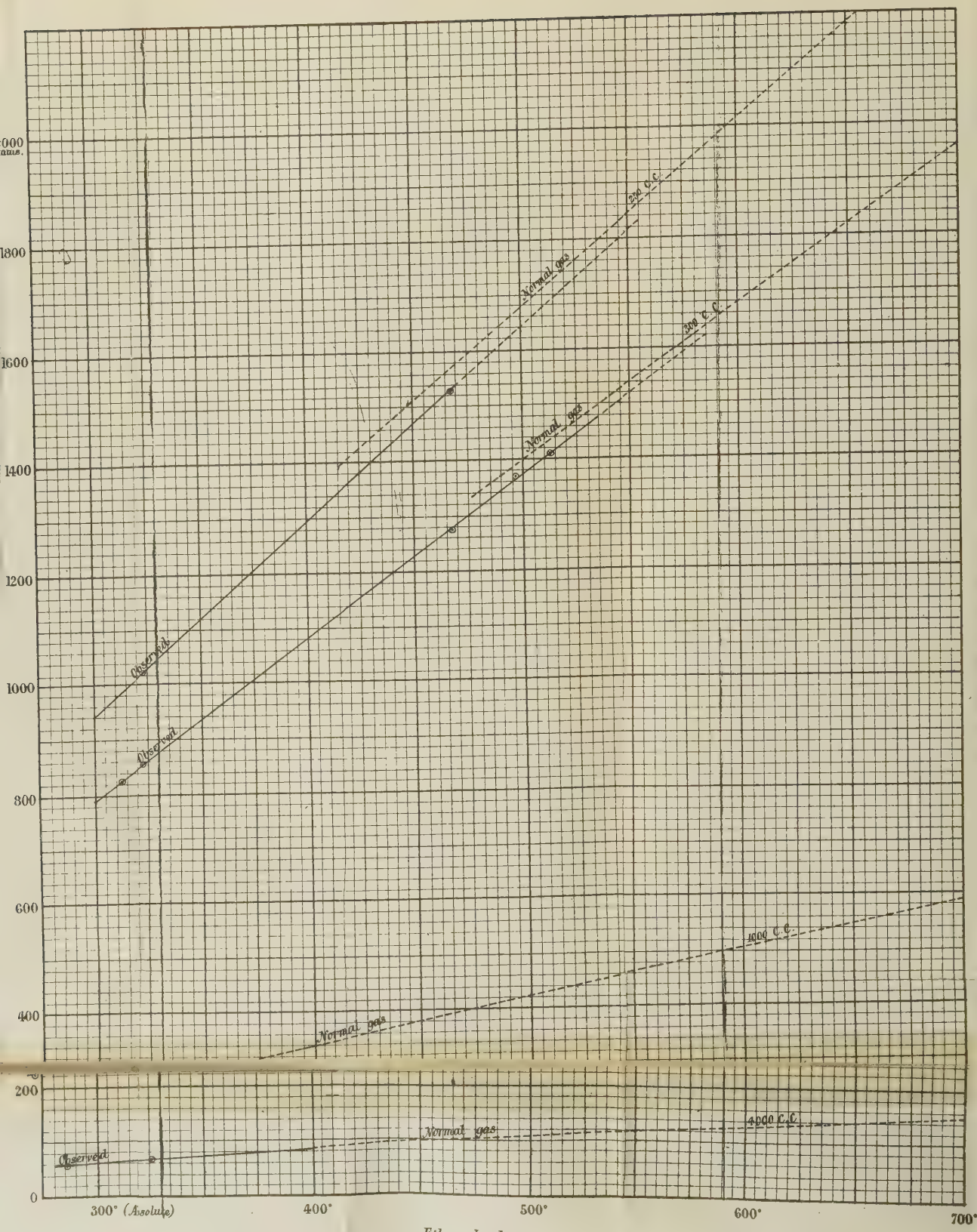

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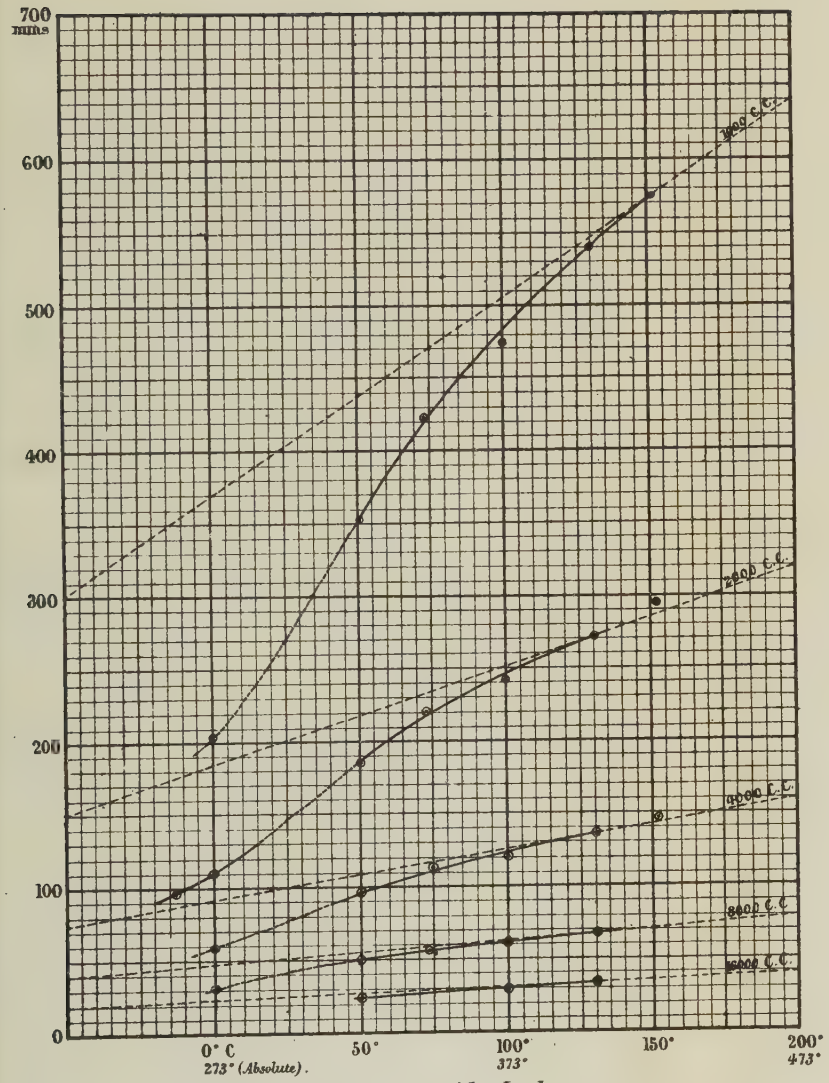

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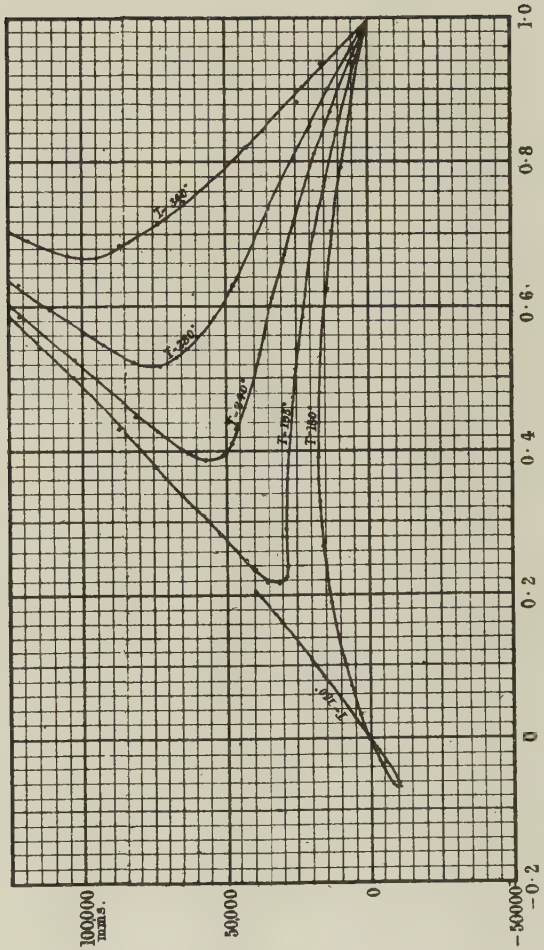
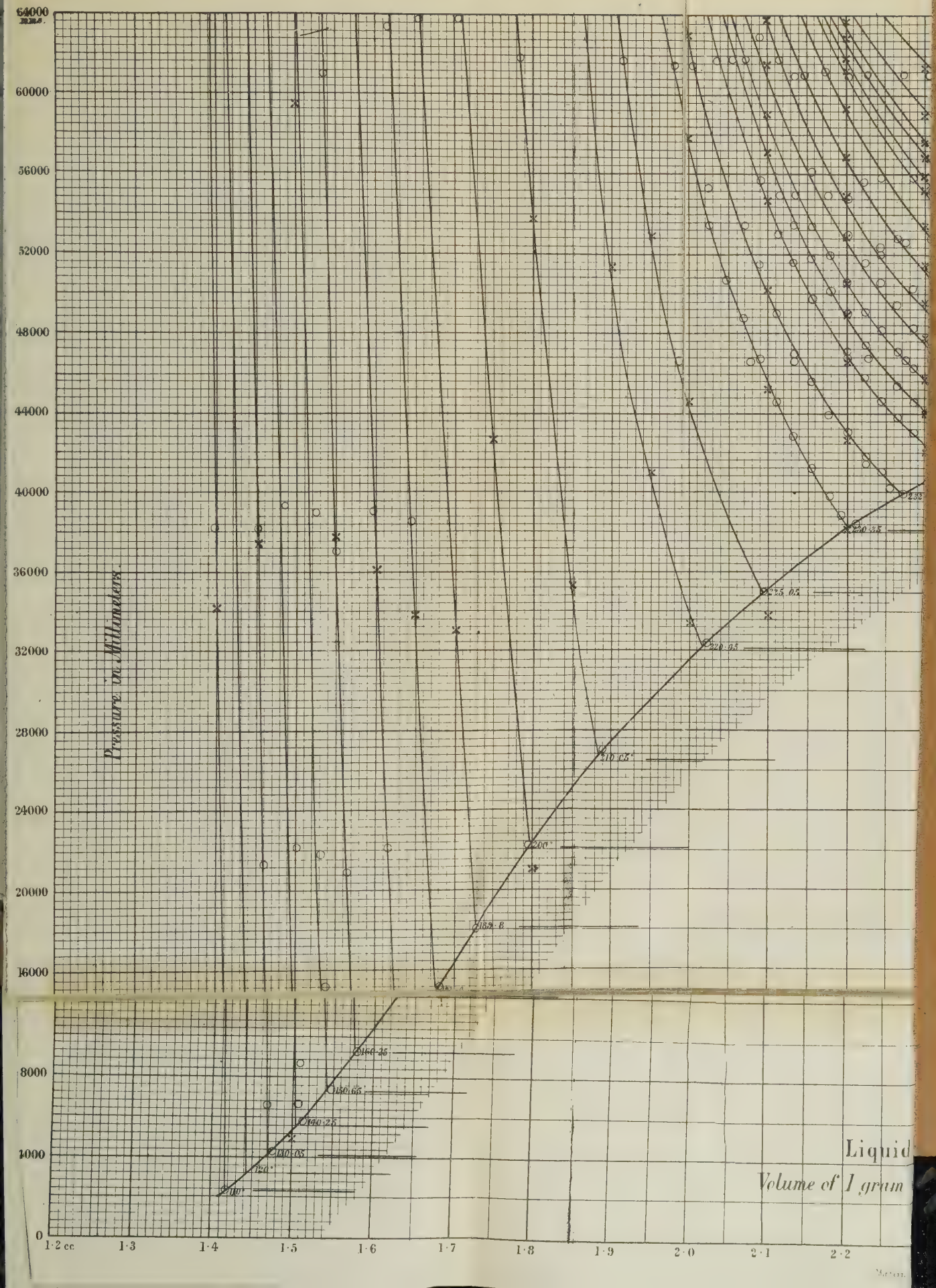
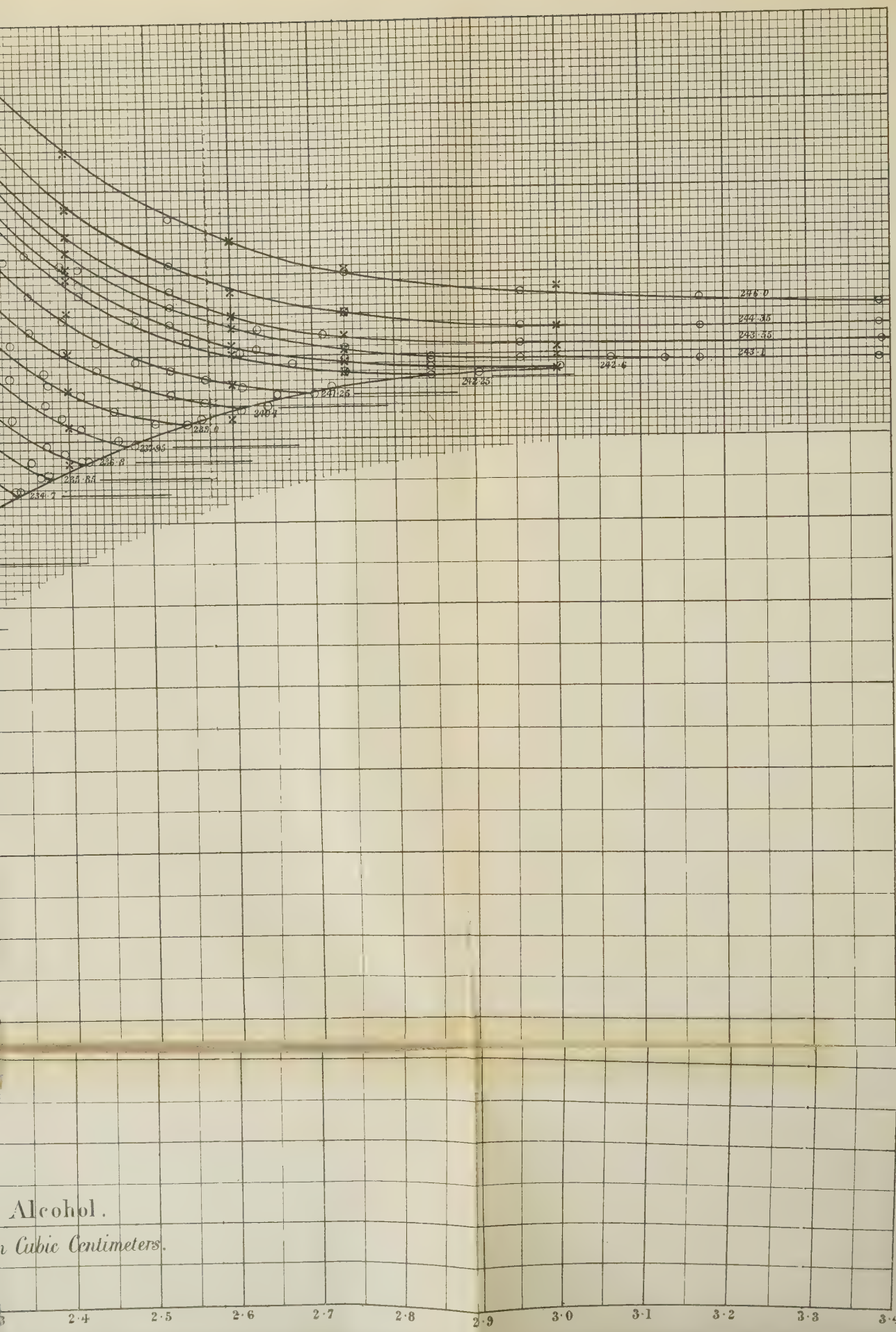
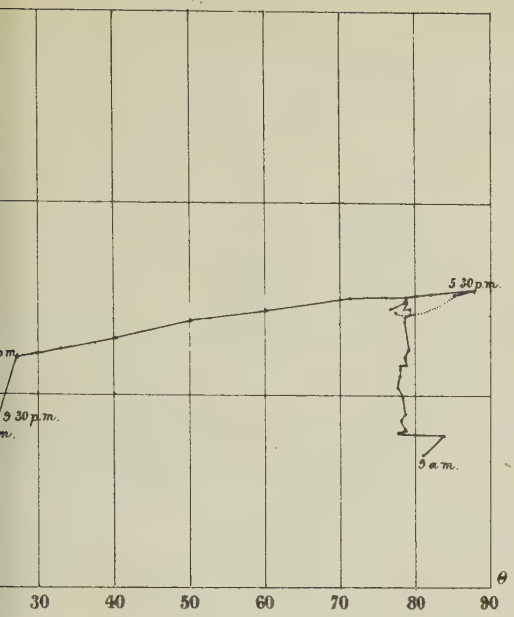


Mintern Bros. lith.


64000
60000
56000
52000
48000
44000
40000
36000
32000
28000
24000
20000
16000
8000
4000
0
Pressure in Millimeters.
1·2 cc
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
Liquid
Volume of 1 grm
232
220·35
225·05
220·95
210·65°
200°
188·8
160·25
150·65
140·25
130·05
120°
110°


246·0
244·35
243·35
243·1
242·6
242·25
241·25
240·4
239·0
237·95
236·8
235·85
234·7
Alcohol.
Cubic Centimeters.
2·4
2·5
2·6
2·7
2·8
2·9
3·0
3·1
3·2
3·3
3·4

April 25th



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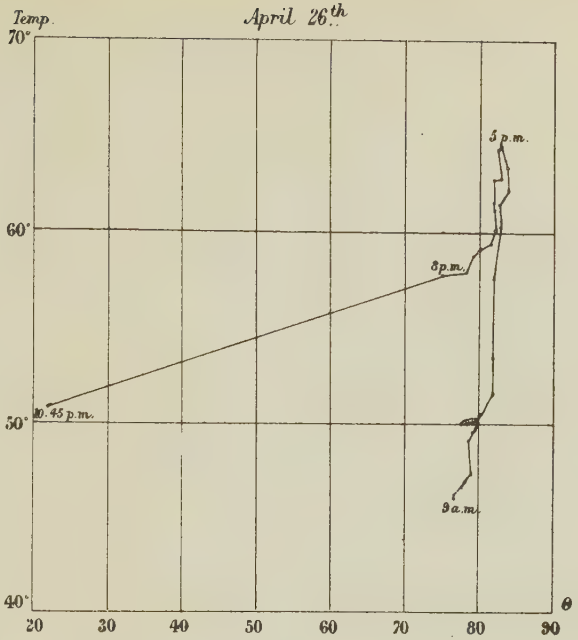

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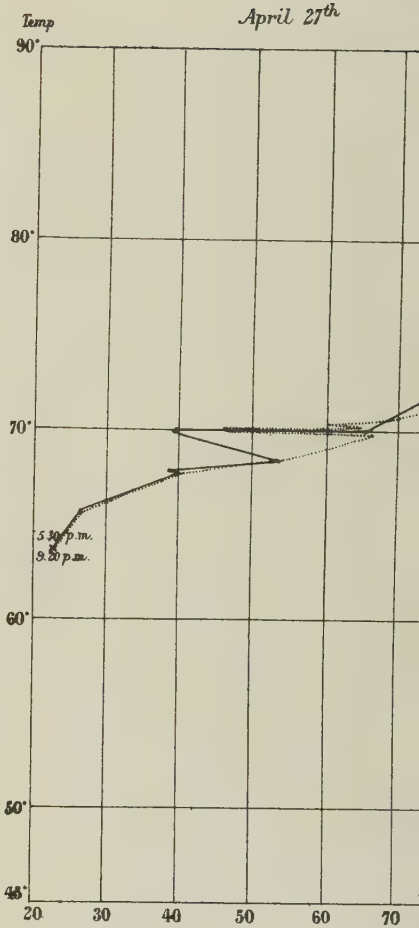

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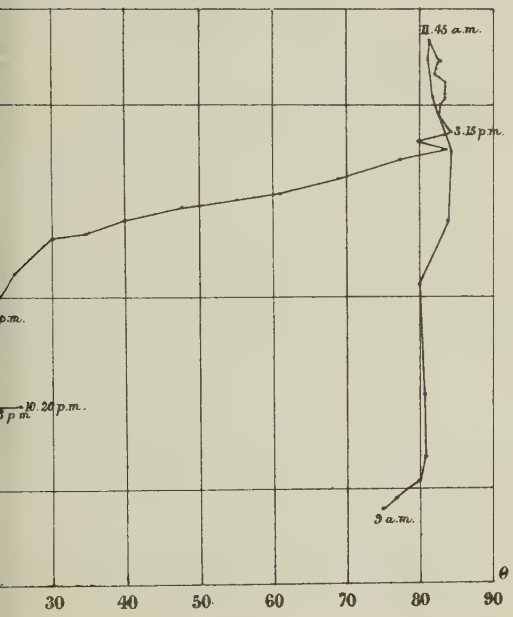

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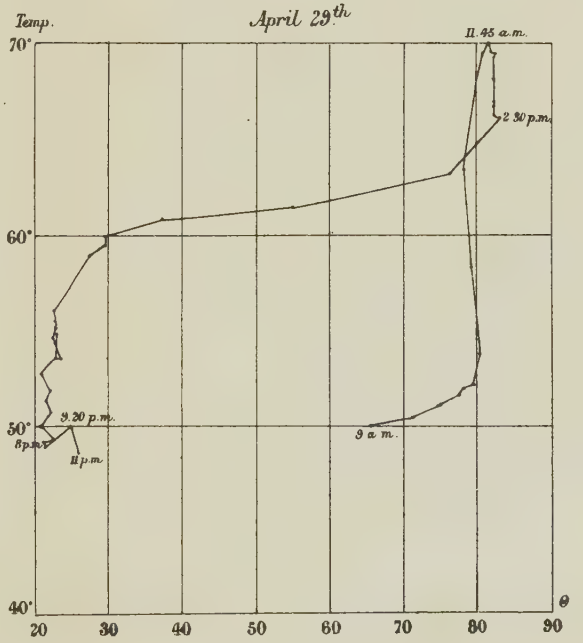
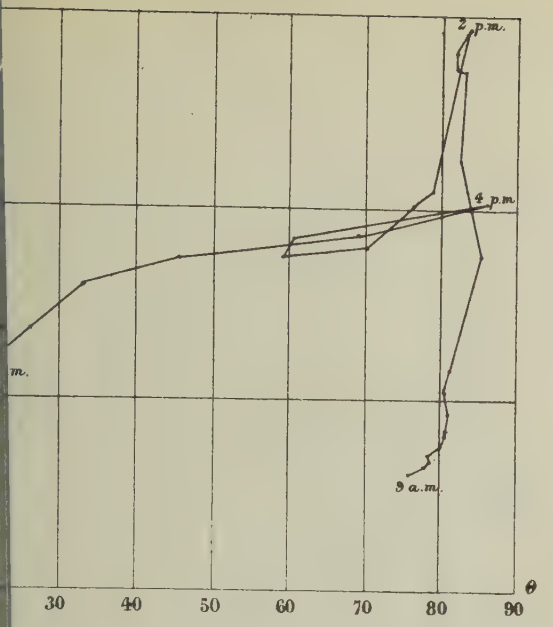


Mintern Bros lith.

May 2nd



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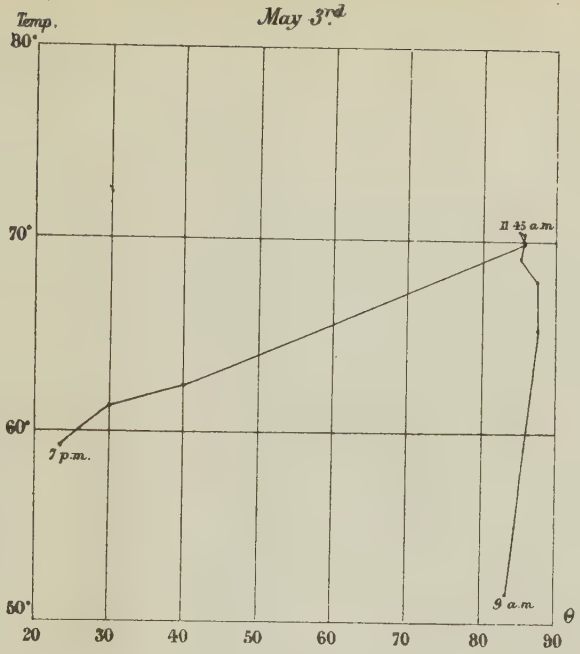

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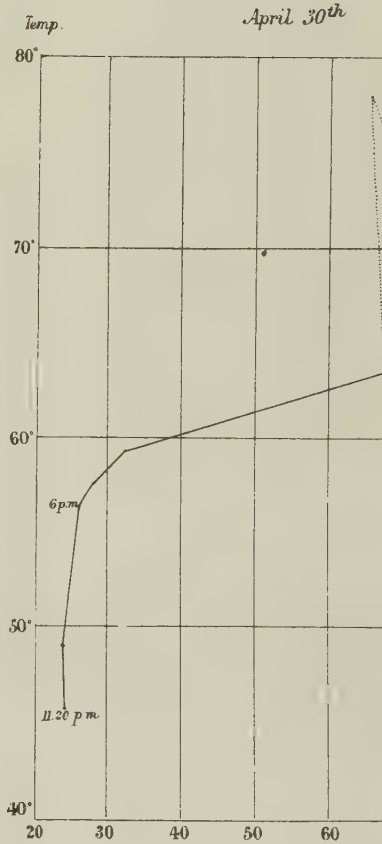

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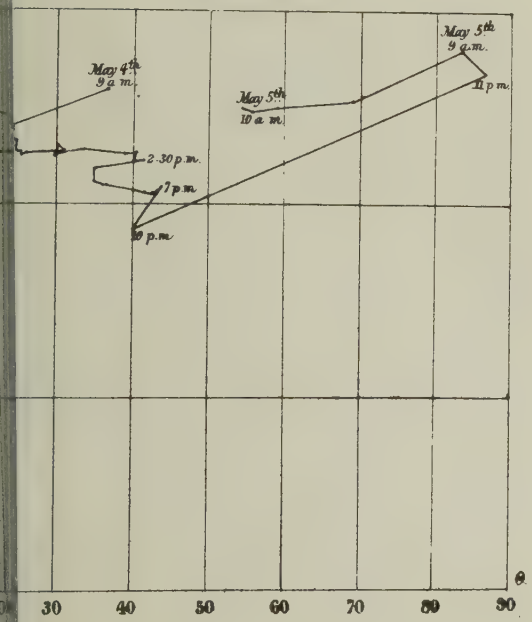
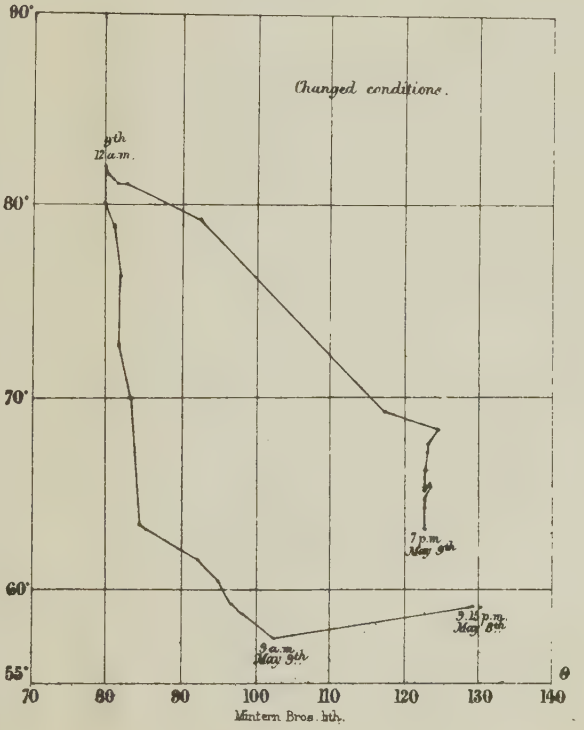


May 8th~9th



Mintern Bros. lith.

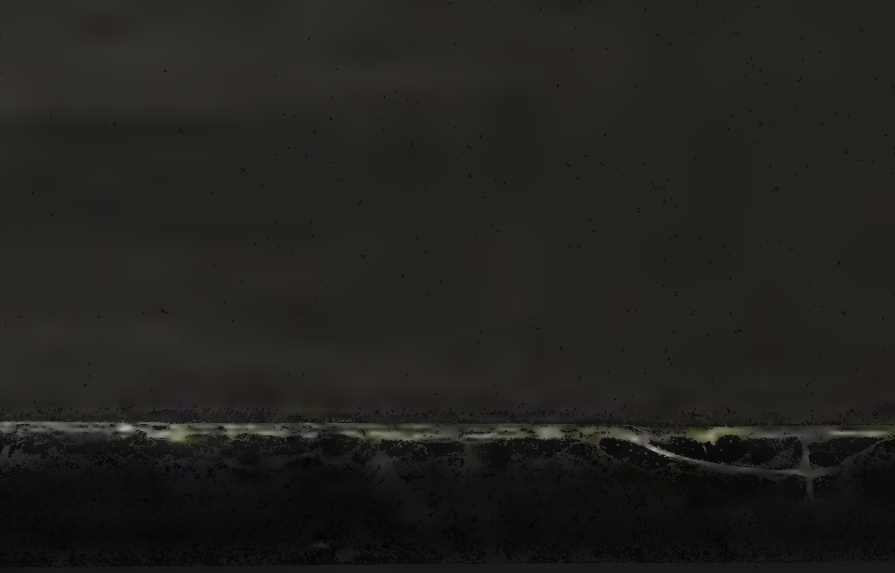


Fig. 1.

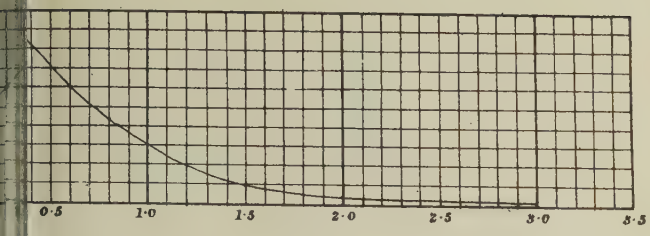
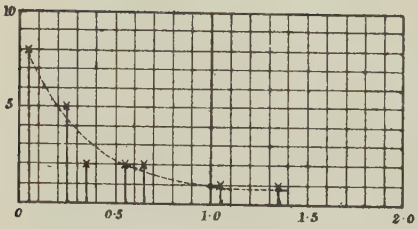


Fig. 2.



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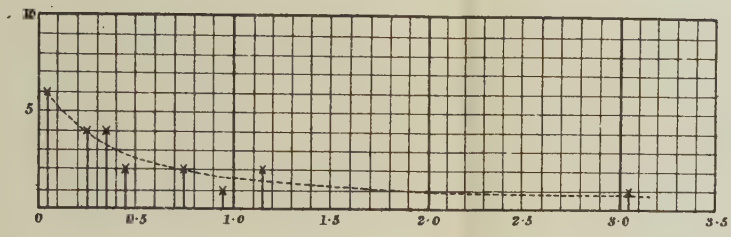

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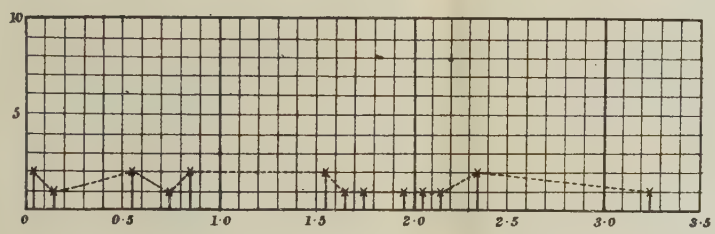

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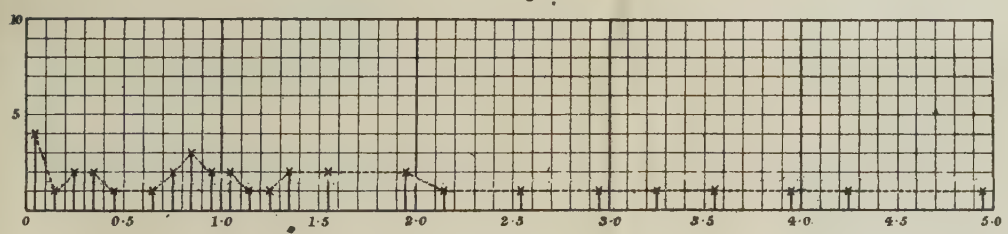

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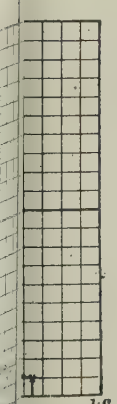

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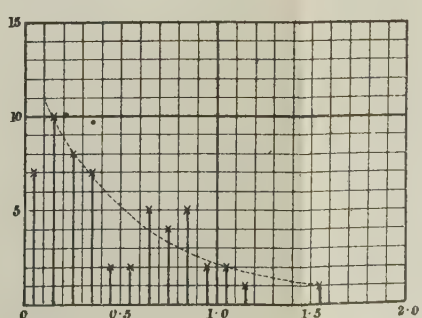

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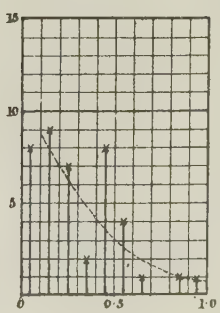


Mintern Bros. lith.

Fig. 1.

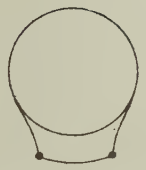
Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.



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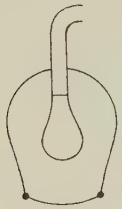

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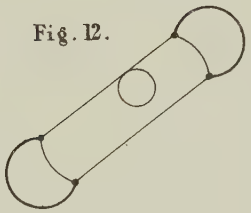

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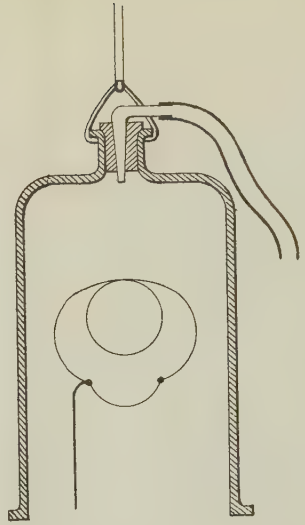


Fig. 9.

Fig.

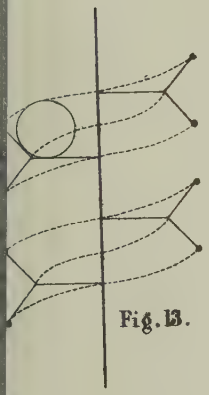
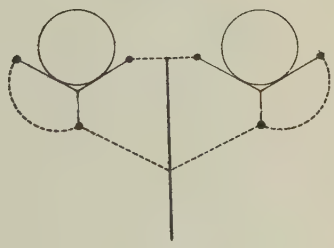


Fig. 13.

Fig. 14.



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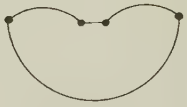

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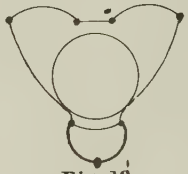

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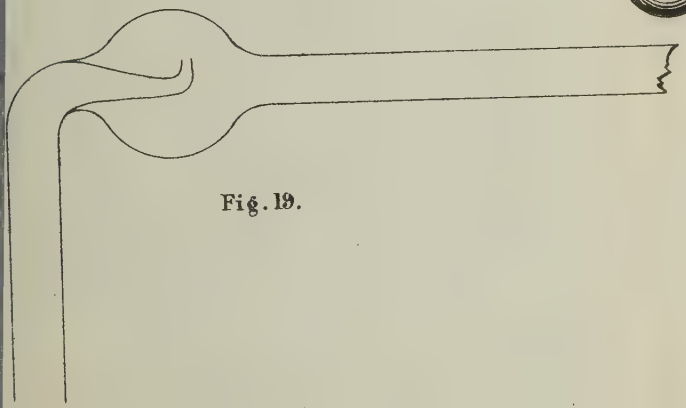

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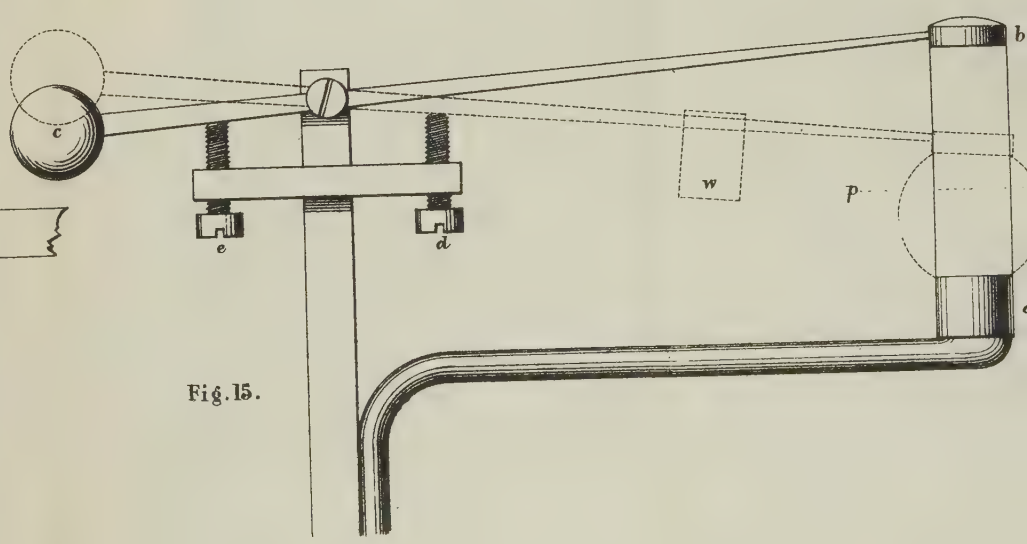


Fig. 15.

Mintern Bros. lith.

Fig. 3.

Value of L/R
Value of C.o
Current.
R1
Q1
R2
Q2
T2
T1
P3
P2
P1
Time Ratio
Time

Fig. 4.

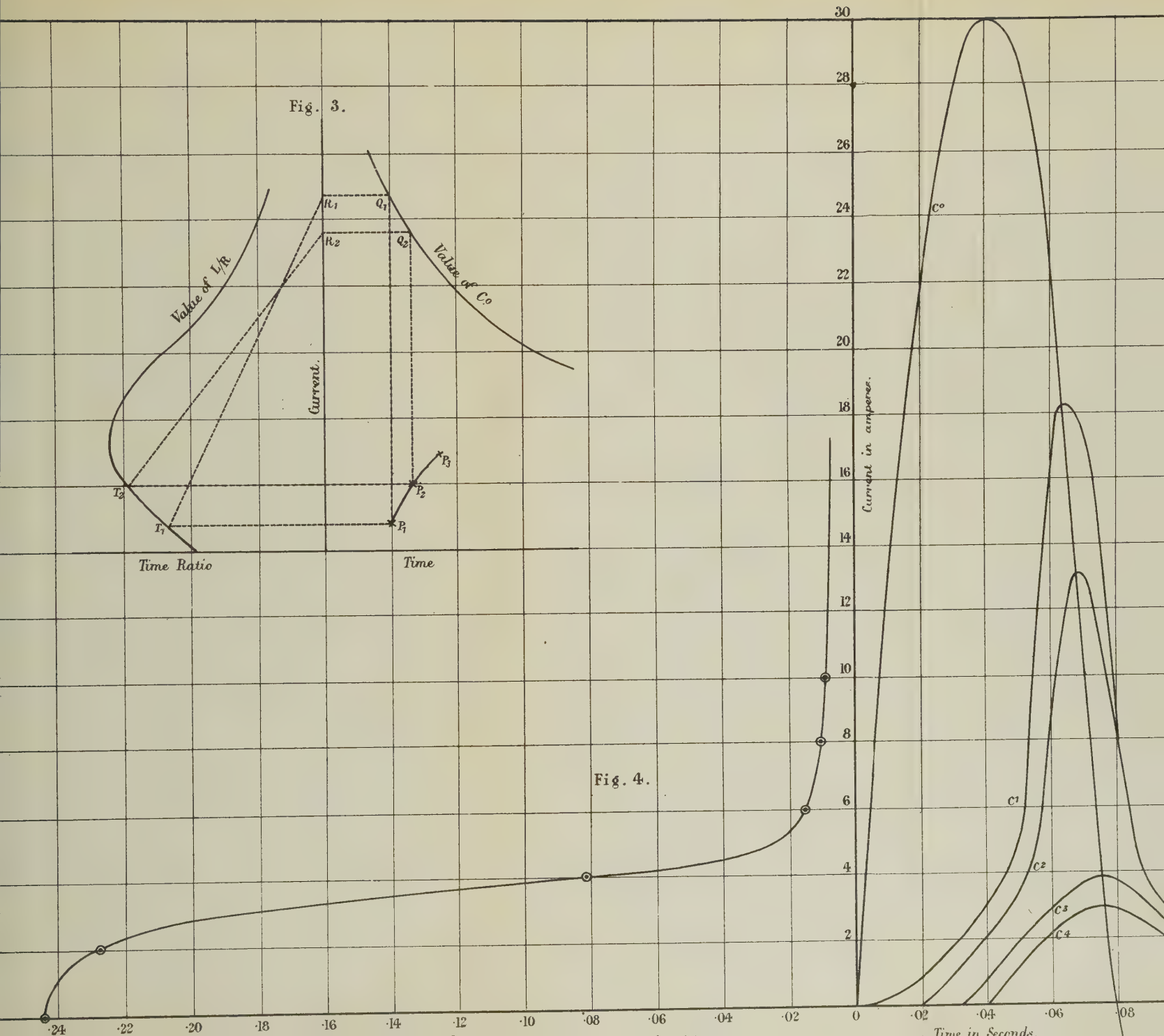
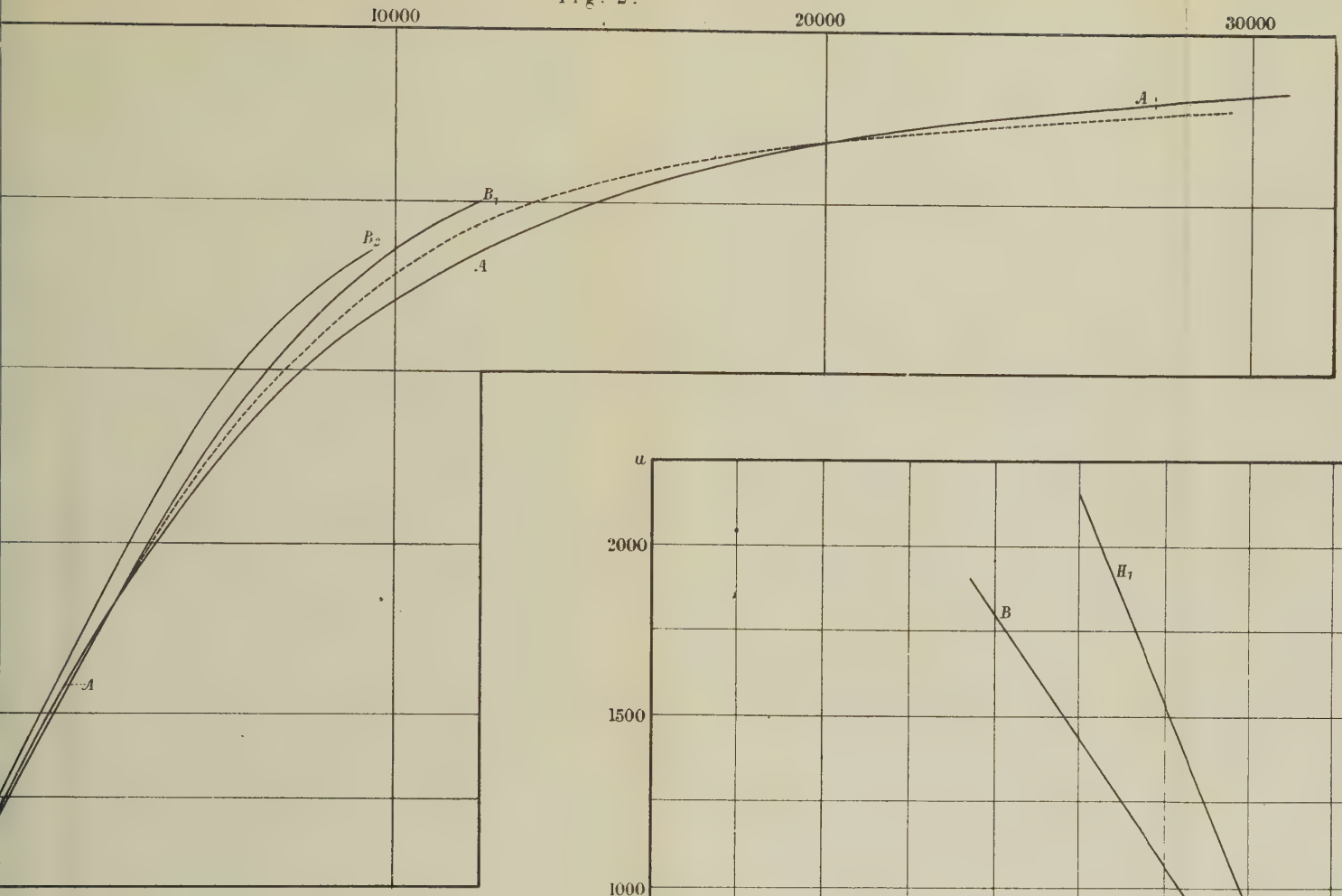
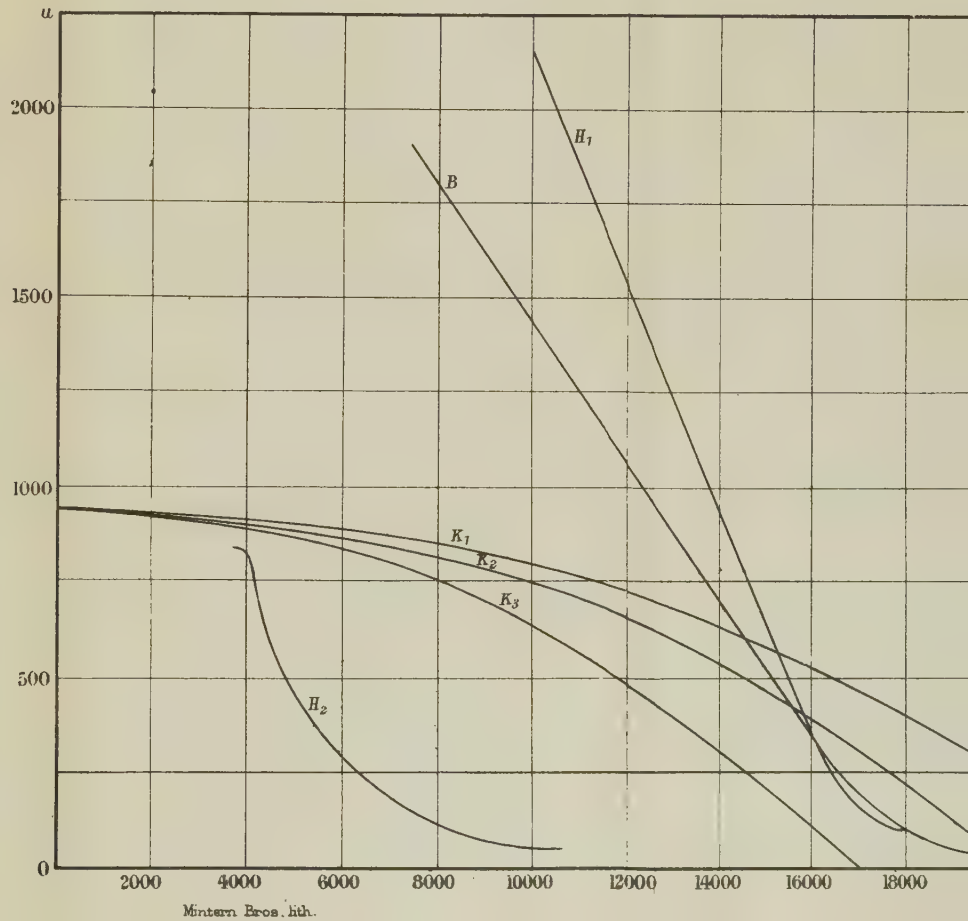

30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
Current in amperes.
C°
C¹
C²
C³
C⁴
·24
·22
·20
·18
·16
·14
·12
·10
·08
·06
·04
·02
0
·02
·04
·06
·08
Time in Seconds.

Fig. 2.





Mintern Bros. lith.

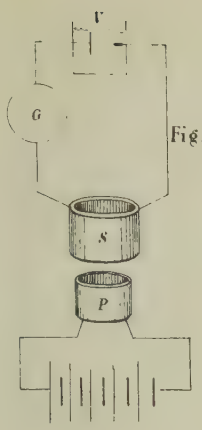


Fig. 2

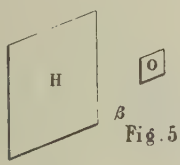


Fig. 5.

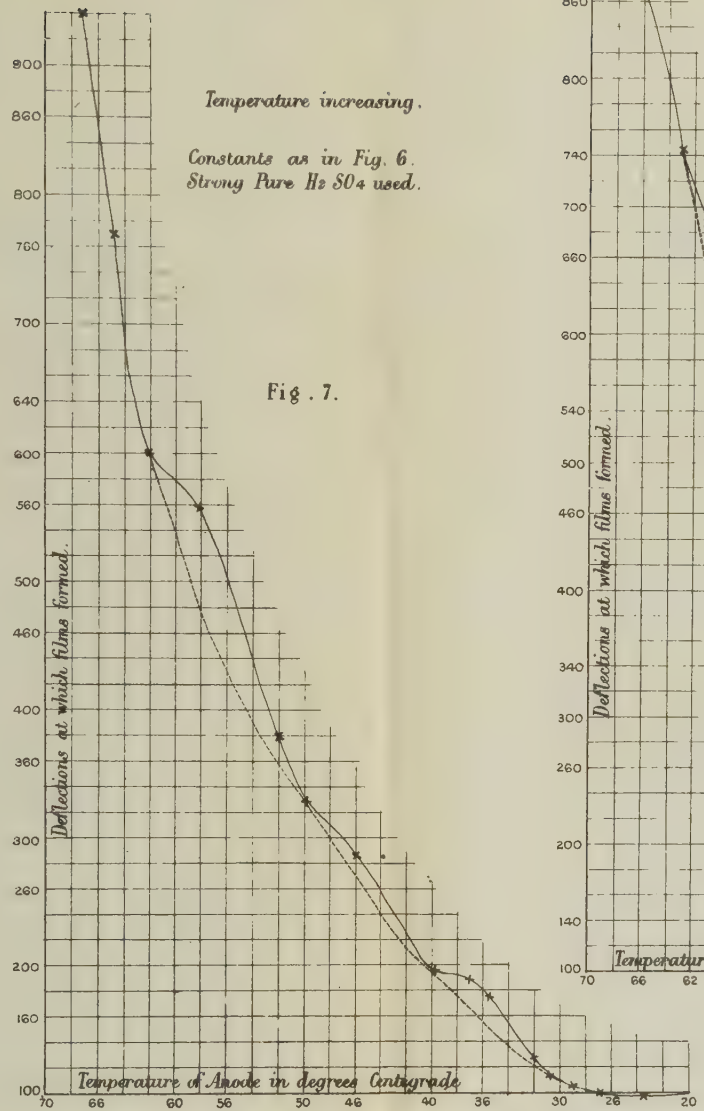

Temperature increasing.
Constants as in Fig. 6.
Strong Pure H₂ SO₄ used.
Deflections at which films formed.
Temperature of Anode in degrees Centigrade

Fig. 7.

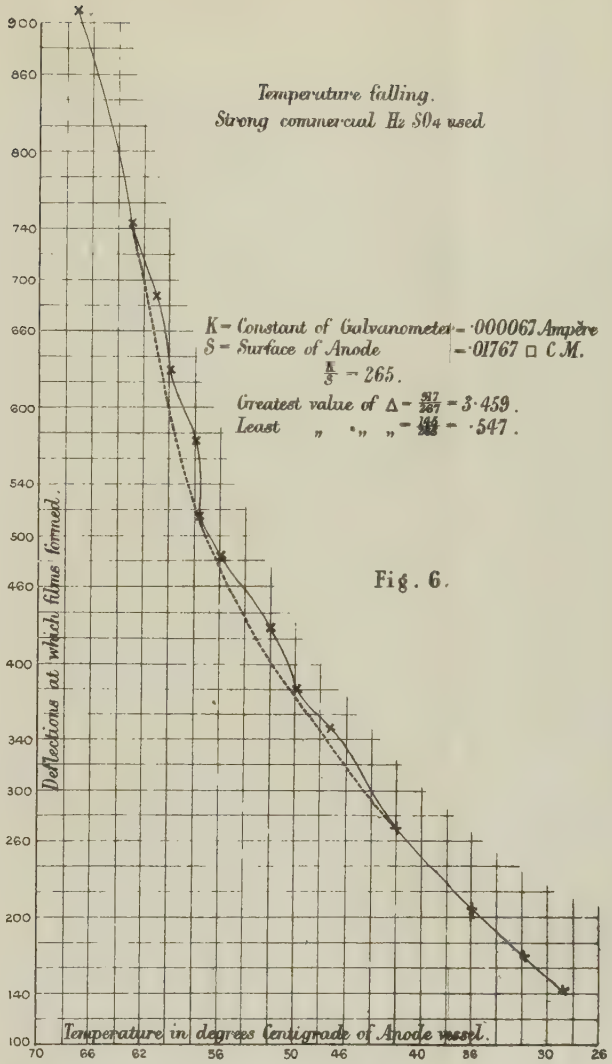

Temperature falling.
Strong commercial H₂ SO₄ used
K = Constant of Galvanometer = ·000067 Ampère
S = Surface of Anode = ·01767 □ C.M.
K/S = 265.
Greatest value of Δ = 317/267 = 3·459.
Least „ „ „ = 141/258 = ·547.
Deflections at which films formed.
Temperature in degrees Centigrade of Anode vessel.

Fig. 6.

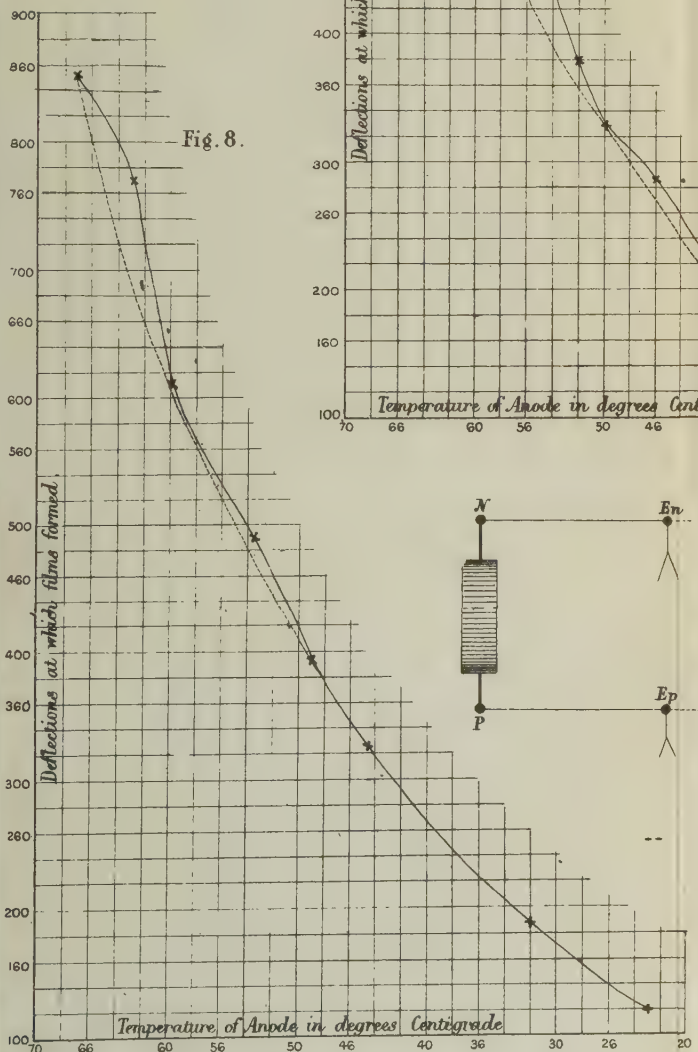


Fig. 8.

Temperature falling.
Constants as before
Strong Pure H₂ SO₄ used.

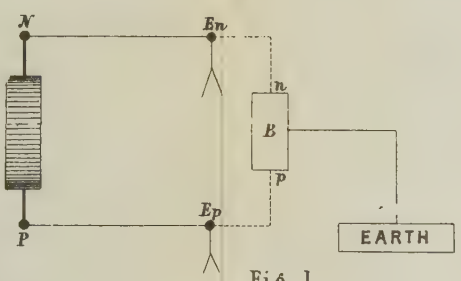


Fig. 1.

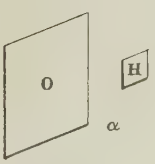


Fig. 4.

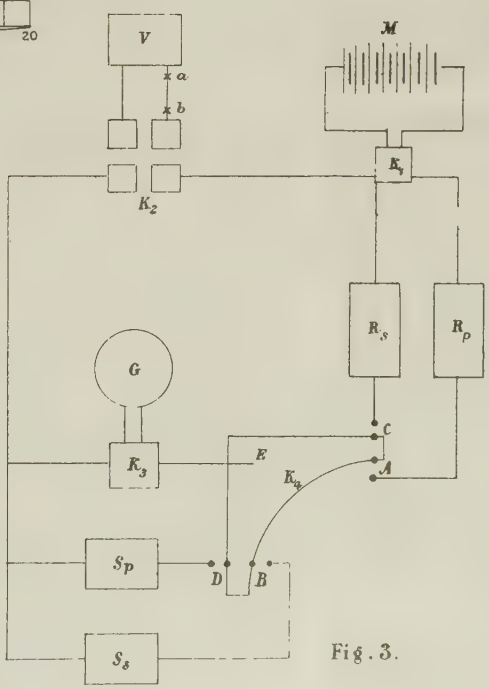
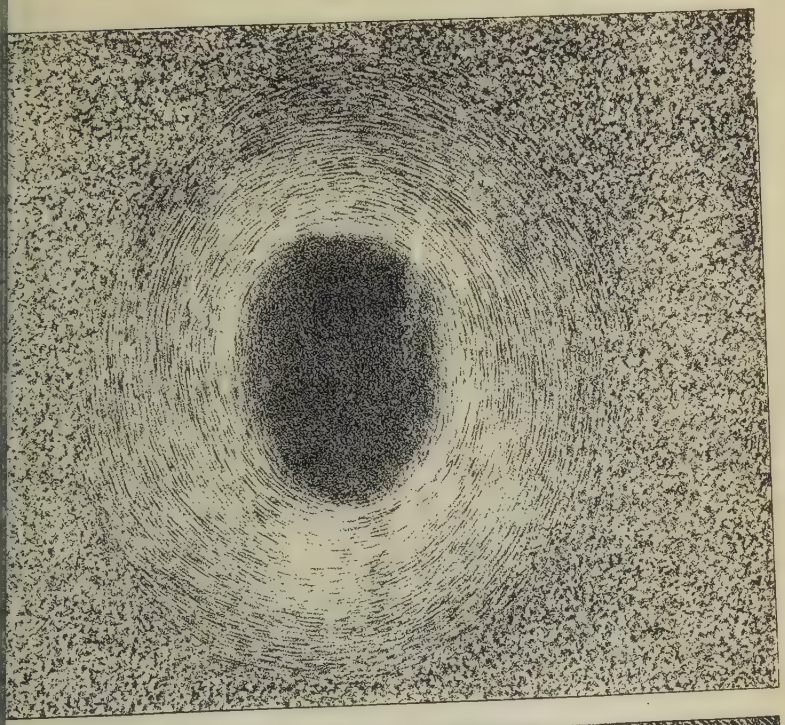
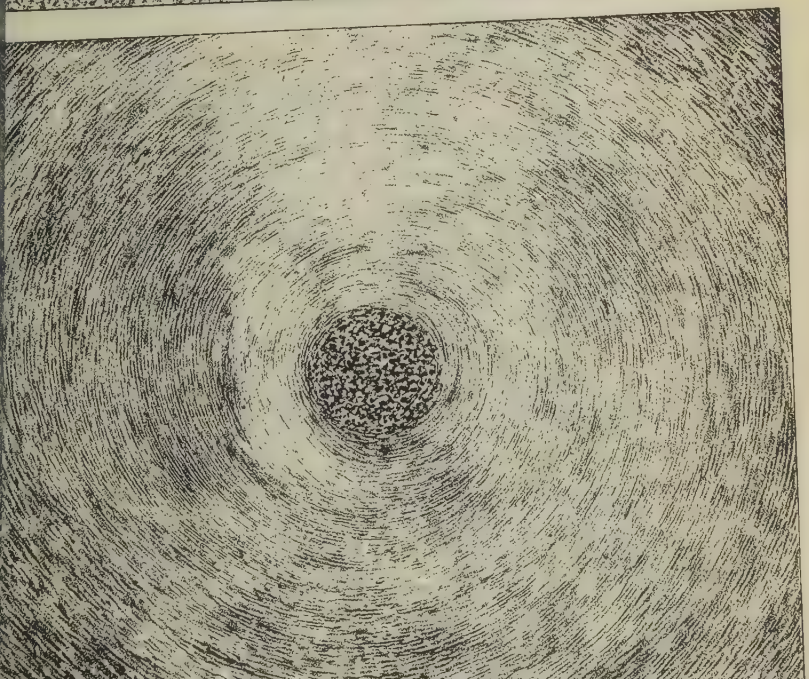


Fig. 3.

Mintern Bros. lith.





PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1887–88.

February 12th, 1887.

Prof. Balfour Stewart, President, in the Chair.

The following was elected a Member of the Society:—

Mr. John Brown.

The following communication was made:—

"On the Tenacity of Spun Glass." By Messrs. E. Gibson and R. Gregory.

February 26th, 1887.

Prof. W. G. Adams, Vice-President, in the Chair.

The following were elected Members of the Society:—

Mr. C. S. Galbenkian; Prof. W. Stroud.

The following communications were made:—

"Note on Prof. Carey Foster's Method of Determining the Coefficient of Mutual Induction of two Coils." By Mr. James Swinburne.

"On the Determination of Coefficients of Mutual Induction by an Earth Inductor and a Ballistic Galvanometer." By Mr. R. H. M. Bosanquet.

"On Evaporation and Dissociation.—Part VI. The Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures." By Prof. W. Ramsay and Dr. Sydney Young.

March 12th, 1887.

Prof. G. Carey Foster, Vice-President, in the Chair.

The following communications were made :—

"On the Electrical Conductivity of Vertically Suspended Wires." By Mr. Shelford Bidwell.

"A Lecture Experiment on Self-Induction." By Mr. Shelford Bidwell.

"A Lecture Experiment for proving the Law connecting the Capacity of an Electric Condenser with the Distance between its Coatings." By Profs. Ayrton and Perry.

"Note on Magnetic Resistance." By Profs. Ayrton and Perry.

March 26th, 1887.

Prof. Balfour Stewart, President, and afterwards Prof. W. G. Adams, Vice-President, in the Chair.

The following was elected a Member of the Society :—

M. Edmond van Aubel.

The following communication was made :—

"On the Production and Properties, and on some suggested Uses of the Finest Fibres." By Mr. C. Vernon Boys.

April 23rd, 1887.

Prof. W. G. Adams, Vice-President, in the Chair.

The following communications were made :—

"On Delicate Calorimetrical Thermometers; and on the Expansion of Thermometer Bulbs under Pressure." By Prof. S. U. Pickering.

"Note on Magnetization." By Mr. R. H. M. Bosanquet.

"On a Thermodynamical Relation." By Prof. W. Ramsay and Dr. Sydney Young.

May 14th, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

The following was elected a Member of the Society:—

Mr. T. Mather.

The following communications were made:—

"On a Modification of a Method of Maxwell's for Measuring the Coefficient of Self-Induction." By Mr. E. C. Rimington.

"On the Production of Sudden Changes of Torsion in a Wire by Changes of Temperature." By Mr. R. H. M. Bosanquet.

"On a Magnetic Potentiometer." By Mr. A. P. Chattock.

May 28th, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

The following communications were made:—

"On Transformers for Electrical Distribution." By Prof. S. P. Thompson.

Prof. Ayrton exhibited an experiment illustrating the principle of Transformers.

"On the Magnetic Torsion of Iron Wires." By Mr. Shelford Bidwell.

June 11th, 1887.

Mr. Shelford Bidwell, Vice-President, in the Chair.

The following communications were made:—

Exhibition of Puluj Vacuum Tubes." By Mr. Warren De La Rue.

"Note on Beams fixed at both Ends." By Profs. Ayrton and Perry.

"Note on MM. Vaschy and De la Touanne's Method of Determining Coefficients of Mutual Induction." By Prof. Carey Foster.

"Note on the Relation between the Angle through which a Twisted Steel Strip is Uncoiled, and the Load." By Prof. J. Perry.

June 25th, 1887.

Mr. Shelford Bidwell, Vice-President, in the Chair.

The following communications were made :—

"Note on Magnetic Resistance." By Profs. Ayrton and Perry.

"On Sounding Coils." By Prof. W. Stroud and Mr. J. Wertheimer.

"On the Comparison of Electrical Capacities." By Mr. E. C. Rimington.

"On the Effects of Change of Temperature in Twisting or Untwisting Wires which have suffered Permanent Torsion." By Mr. H. Tomlinson.

"On Permanent-magnet Ammeters and Voltmeters with Invariable Sensibility." By Profs. Ayrton and Perry.

November 12th, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

The following was elected a Member of the Society :—

Lieutenant R. H. S. Bacon, R.N.

The following communications were made :—

"On a Geometrical Method of Determining the Conditions of Maximum Efficiency in the Transmission of Power by Alternating Currents." By Mr. T. H. Blakesley.

"A Lecture Experiment on the Velocity of Sound." By Prof. A. W. Rücker.

November 26th, 1887.

Prof. Balfour Stewart, President, in the Chair.

The following was elected a Member of the Society :—

Asutosh Mukhopadhyay, M.A., F.R.A.S.

The following communications were made:—

"On the Analogies of Influence- and Dynamo-Machines." By Prof. S. P. Thompson.

"On the Effect produced on the Thermoelectric Properties of Iron when under Stress or Strain by Raising the Temperature to Bright Red." By Mr. H. Tomlinson.

"On a Method of Discriminating between Real and Apparent Coincidences of the Lines of Different Spectra; with some Applications." By Mr. E. F. J. Love.

December 10th, 1887.

Prof. W. E. Ayrton, Vice-President, in the Chair.

The following were elected Members of the Society:—

Mr. C. A. Carus-Wilson; Mr. W. E. Sumpner, B.Sc.

The following communications were made:—

"On the Optical Properties of Phenyl-thio-carbimide." By Mr. H. G. Madan.

"On the Recalescence of Iron." By Mr. H. Tomlinson.

"On the Rotation of a Copper Sphere and of Copper-wire Helices when freely suspended in a Magnetic Field." By Dr. Shettle.

January 28th, 1888.

Prof. W. G. Adams, Vice-President, in the Chair.

The Chairman reported the death of the President, Prof. Balfour Stewart, which took place on the 18th December, 1887.

The following communications were read:—

"On the Effect of Magnetization on the Thermoelectric Properties of Bismuth." By Mr. H. M'Leod.

"On the Influence of Magnetism and Temperature on the Electric Properties of Bismuth, and of its Alloys with Tin and Lead." By M. E. van Aubel.

"On a Water-Dropping Influence-Machine." By Prof. S. P. Thompson.

"On the Price of the Factor of Safety in Lightning Rods." By Prof. S. P. Thompson.

"On the Optical Demonstration of Electrical Stress." By Prof. A. W. Rücker and Mr. C. V. Boys.

Annual General Meeting.

February 11th, 1888.

Dr. Gladstone, F.R.S., Vice-President, in the Chair.

The following Report of the Council was read by the Chairman :—

At the Annual General Meeting last year the Council, in presenting their Report to the Society, had to record the death of Dr. Guthrie, who had taken a leading part in the formation and work of the Society, and who died only eight months after vacating the Presidential Chair. This year the Council regret to have to report the death of Dr. Balfour Stewart, who would to-day, had he survived, have completed his two years' term of office as President. Dr. Stewart was well known to most of us ; and, though living at a considerable distance from London, was not unfrequently present at and presided over our Meetings. He died very suddenly on the 18th of December last, at Ballymagarvey, near Dublin, whither he had gone to spend Christmas with his family.

The Council have also to record the deaths of Professor Kirchhoff, of Berlin, who was elected an Honorary Member of the Society in 1879 ; of Mr. Coutts Trotter, Fellow of Trinity College, Cambridge ; and of Prof. Humpidge, of University College, Aberystwith.

Since our last Annual Meeting a Bust of the late Dr. Guthrie, kindly presented to the Society by Mrs. Guthrie, has been placed on a bracket in the room in which our Meetings are held.

The Council consider that the work of the Society during the past year has been satisfactory. The Meetings have been well attended, and have often been prolonged beyond the limits usually assigned to the scientific business of a Meeting. The papers brought before us have not fallen short, either in number or general interest, of those of previous years, and have frequently given rise to useful discussions. As many of these communications, however, are of the nature of notes or lecture experiments, or refer to investigations

published elsewhere, the amount of printed matter in the quarterly parts of our 'Proceedings' is somewhat less than was the case last year. The Council would again impress upon Members the importance of bringing their original researches in the first instance before this Society. The advantages they thereby gain are early and wide publication of their papers, and an ample supply of extra copies furnished at the expense of the Society

The Council regret to announce that the number of Members has not increased during the last year. Our losses by death and withdrawal have only just been compensated by the new Members elected. There are, doubtless, many students of Physics in this country, and others interested in the objects of our Society, who would be willing to join us, if they were aware of the advantages which we offer them.

The Council have determined to issue from time to time translations of important Physical Memoirs published abroad. In deciding to enter upon this undertaking the Council have been influenced by the consideration that there is not at present any channel through which the longer and more elaborate publications of Continental Physicists become accessible to a large number of their English fellow-workers. The extent of the Society's action in this direction will chiefly depend upon the amount of funds available for the purpose, for the Society can hardly hope to do more than make a selection among the many valuable foreign memoirs which it would be desirable to republish in this country.

These translations will be printed and got up uniformly with the Proceedings of the Physical Society,' but will be paged separately. The first Part, of over 100 pages, containing a series of five papers by Professor von Helmholtz, on the Application of the Principles of Thermodynamics to Chemical Action and Electrolysis, is in an advanced state of preparation, and will be issued to Members very shortly. It will be followed as soon as practicable by a translation of Hittorff's two memoirs on the Discharge of Electricity through Rarefied Gases; and by a translation of Puluj's memoir on Radiant Electrode-Matter, which has been kindly promised to the Society by Dr. De La Rue.

Negotiations are now in progress for the final revision and production of the translation of Volta's works which the Society has undertaken.

Since the last Annual Meeting the Bye-Laws have been amended in such a way as to allow us to elect, as Members of the Society,

gentlemen residing abroad, who are personally unknown to our Members, but otherwise qualified for election. Under the new rule two new Members have been elected—one residing in Belgium, the other in India.

In order to facilitate the investment of the Society's funds, the Council in June last resolved to procure a Seal for the Society, under which future investments might be made. A small Committee was appointed to consider the matter, and a simple design was selected and approved by the Council. The Seal will remain in the custody of the Treasurer and one other Member of Council, and future investments will be made in their name under the Corporate Seal.

The Library now contains about 1000 volumes, consisting largely of Periodicals and the Proceedings of Learned Societies. The Council wish it to be known that the Library is open to all Members of the Society for consultation of books, and that Members may take away bound volumes.

The following additions to the Library have been made during the past year:—

Journal of the Society of Arts.
Quarterly Journal of the Royal Meteorological Society.
Proceedings of the Academy of Natural Sciences, Philadelphia.
Journal of the Society of Telegraph Engineers.
Proceedings of the Institute of Mechanical Engineers.
Journal of the College of Science, Japan.
Journal of the Physical and Chemical Society of Russia.
Johns Hopkins University Circular.
Séances de la Société Française de Physique.
Proceedings of the Cambridge Philosophical Society.
Proceedings of the Royal Institution.
Journal and Proceedings of the Royal Society, N. S. Wales.
Transactions of the Seismological Society, Japan.
Crónica Cientifica.
Electrical Review.
Beiblätter der Physik und Chemie.
Annalen der Physik und Chemie.
Journal de Physique.
Scientific News.
The Naturalists' Monthly.
Electrical Plant.
Ingeniero y Ferretero Español.
Indian, Colonial, and Foreign Engineer and Builder.

Kew Observatory Report, 1887.
Catalogue of the Library of the Institution of Mechanical Engineers.
List of Members of the Royal Institution.

The Council have approved the following

RULES FOR THE REGULATION OF THE LIBRARY.

1. Books taken from the Library must be returned within three months, when they may be again borrowed unless wanted by another Member.
2. If a book in possession of one Member is wanted by another, it must be returned within a week; but if it has not been borrowed for more than a fortnight, it may be retained for a period of three weeks from the time of borrowing.
3. Unbound books or parts of periodicals may be consulted in the Library, but may not be taken away.
4. Books cannot be sent out; they must, in all cases, be taken away by a Member, or by some person with his written authority, after which such Member will be responsible for their condition and safety.
5. In no case may books be taken away unless the particulars are entered in a book kept for the purpose.
6. The total number of books that a Member may have out at any one time is limited to four.

Fines.

1. A fine of One Shilling per volume shall be imposed for every week, or fraction of a week, that a book is detained beyond the time fixed for its return (notice being sent); and the use of the Library shall be withdrawn till the fine is paid in full. Money received as fines shall be used for the benefit of the Library.
2. If a borrowed book be lost or damaged, the borrower shall replace it, or pay the full value of the set to which it belongs (such value to be estimated by the Council), or any sum less than the full value, at the discretion of the Council.

NOTICES OF DECEASED MEMBERS.

Dr. BALFOUR STEWART was born in Edinburgh on November 1, 1828. His uncle, Dr. Cloaston, the minister of Stanwick, was a well-known naturalist and meteorologist. Having studied for a short time at each of the Universities of St. Andrews and Edin-

burgh, Stewart began practical life in a mercantile office. In the course of a business voyage to Australia, his particular taste for physical science developed itself; and his first published papers, "On the Adaptation of the Eye to Different Rays," and "On the Influence of Gravity on the Physical Condition of the Moon's Surface," appeared in the 'Transactions of the Physical Society of Victoria.' On his return he gave up business for science, and resumed study under Kelland and Forbes, to the latter of whom he soon became assistant. During this period, in 1858, Stewart was led to his well-known extension of Prévost's 'Law of Exchanges,' a most remarkable and important contribution to the theory of radiation. He seems to have been the first to suggest, from a scientific standpoint, that radiation is not a mere surface phenomenon. With the aid of Forbes's apparatus, he fully demonstrated the truth of the conclusions to which he had been led by theory; and the award of the Rumford Medal by the Royal Society, some years later, showed that his work had been estimated at its true value. In fact, his proof of the necessary equality between the radiating and the absorbing powers of every substance remains to this day the simplest, and therefore the most convincing, that has yet been given.

On the death of Mr. Welsh, in 1859, Balfour Stewart was selected to succeed him as Superintendent of the Kew Observatory, and held the office until 1871. During these years he maintained and improved upon the memorable labours of Ronalds and Welsh. Every species of inquiry which had to be carried out at Kew—whether it consisted in the testing of thermometers, sextants, pendulums, aneroids, or dipping-needles, the recording of atmospheric electricity, the determination of the freezing-point of mercury or the melting-point of paraffin, or the careful study of the peculiarities of the air-thermometer—received the benefit of his valuable suggestions, and was carried out with his scrupulous accuracy.

In 1867 Stewart was appointed Secretary of the Government Meteorological Committee; and in the following year superintended the erection of the instruments at the several stations of the Meteorological Office—Aberdeen, Armagh, Falmouth, Glasgow, Stonyhurst, and Valencia. At the close of the year 1869 he resigned the Secretaryship of the Meteorological Committee.

In 1870, on his appointment to the Chair of Natural Philosophy in Owens College, Dr. Stewart left Richmond, to take up his residence in the neighbourhood of Manchester; but continued to act as

Superintendent of the Kew Observatory. It was in November of this year that, in one of his journeys between London and Manchester, he met with the railway accident which so nearly proved fatal to him. His thigh was dreadfully crushed; and it was nine months before he could be removed from Harrow, where the disaster occurred. He was permanently lamed, and sustained severe injury to his constitution. From the vigorous activity of the prime of life, he passed in a few months to grey-headed old age. But his characteristic patience was unruffled and his intellect unimpaired.

He was much interested in the phenomena of sun-spots, and their connexion with the earth's magnetism. In 1866 the first set of results obtained from the photo-heliograph was published, at the expense of Dr. Warren De La Rue, under the title of "Researches on Solar Physics," by Messrs. De La Rue, B. Stewart, and B. Loewy. This was followed by papers on Sun-spot areas &c., published in the same manner in 1867 and 1868. The results of these researches were also communicated to the Royal Society.

Of recent years Dr. Stewart's attention had been turned to the difficult problem of terrestrial magnetism and its variations. One of his last papers read before this Society investigated the causes of the solar diurnal variation of the earth's magnetism. In his latest remarks addressed to us, on November 26th, he made reference to this subject, and hinted at the probability that before long many of its obscure phenomena would receive an explanation. The article on "Terrestrial Magnetism" in the new edition of the 'Encyclopædia Britannica' was contributed by him.

Dr. Stewart was elected a Fellow of the Royal Society in 1862, and was awarded the Rumford Medal in 1868. He was President of Section A of the British Association in 1875, at the Bristol Meeting. He was an original Member of our Society.

For two periods he acted as Examiner in Natural Philosophy in the University of London, and he also examined for the University of Edinburgh and other Examining Boards.

When in Richmond, Dr. Stewart was Churchwarden of St. John's Church, School Manager, Superintendent of the Boys' Sunday School, and generally an active coadjutor of the Vicar (Canon J. D. Hales) in parish matters. He was interested, as is well known, in psychical science, and was President of the Society for Psychical Research. The philosophic and speculative tone of his mind was well illustrated in the 'Unseen Universe,' which he wrote in conjunction with Prof. P. G. Tait. This work, which appeared in

1874, excited a profound interest, and passed through many editions. In it the authors combated the view that science and religion are incompatible with each other, and contended, from a purely physical point of view, for the possibility of immortality and a personal God.

As a writer of text-books on Physics Dr Balfour Stewart was very successful. Among these may be mentioned his 'Elementary Treatise on Heat,' published in 1866; 'Lessons in Elementary Physics' (1871); 'Physics' (1878); and 'The Conservation of Energy' (1874). Of his work on 'Practical Physics,' written in conjunction with Mr Haldane Gee, two volumes have already appeared, and the third volume is in an advanced state of preparation.

At Manchester Prof. Balfour Stewart saw the establishment of the Victoria University, and took an active part in the arrangements of the mathematical curriculum.

He died very suddenly at Ballyemgarvey, near Navan, co. Meath, Ireland, on the 19th of last December.

Gustav Robert Kirchhoff, Honorary Member of the Society, was born in Königsberg in March 1824, the son of a lawyer of that town. At eighteen he entered the University of Königsberg, where he attended the mathematical lectures of Richelot, whose daughter he afterwards (1857) married; and studied Physics under Franz Neumann, who, directly or indirectly, has been the teacher and inspirer of almost every mathematical physicist of Germany. At the age of twenty-one, while still a pupil of Neumann, Kirchhoff published his celebrated investigation into the law of electricity in a plane conducting sheet. At twenty-three he took his Doctor's Degree with so much distinction that, as a mark of approval, a fund was awarded to him to defray the cost of a scientific journey to Paris. This was in 1845. Being prevented by the political unrest of the time from carrying out his intended journey, Kirchhoff connected himself with the University of Berlin as Privatdocent. It is noteworthy that in the University, where afterwards his lectures were attended by hundreds of eagerly attentive listeners, the first course announced by him was not delivered for want of an audience. In 1850 Kirchhoff was called to Breslau as Extraordinary Professor of Physics. Here began an afterwards intimate friendship with Bunsen, which influenced in important respects the outward course of Kirchhoff's subsequent life as well as the direction of his scientific activity. On Gmelin's death, Bunsen went to Heidelberg as Professor of Chemistry, and when, in 1854, Jolly

ber Heidelberg for Munich, the Ordinary Professorship of Physics in Heidelberg was by Bunsen's advice offered to Kirchhoff. This post was retained by Kirchhoff for twenty-one years, until he left, in 1875, to accept a call, the third that had been addressed to him, to the University of Berlin. It was in Heidelberg he commenced fellowship with his friend Bunsen, and partly in collaboration with him, that Kirchhoff's researches into the nature of the solar spectrum and the relation to the spectra of the light from terrestrial sources were carried out. These investigations, which have attracted far more general attention than any other part of Kirchhoff's work, supplied the key wherewith, in the hands of Kirchhoff himself, followed by Stokes, Ångström, and others, stores of knowledge have been unlocked concerning the sun and other heavenly bodies which previously had been supposed to be for ever inaccessible. The starting point of these discoveries was the establishment of the relation between the dark lines of the solar spectrum and the bright lines of the spectra of artificial sources of light. Kirchhoff having with Bunsen determined the crystal refrangibility of the dark solar line D and the bright yellow line given by a sodium-flame, was thereby led to the belief that D proved a fixed coincident with, and that the dark or bright appearance of the same line or right from the sun, depended only on whether a brighter line in the place of the dark line previously visible, did thus indeed supervene with different light from the clouds; but when the supervened was dark with dark, but somehow the dark line, instead of being changed to bright, became darker and broader than before. He left the discovery nothing. "That seems to me to go to the root of the matter," he wrote about one experimental question. "I can't help thinking the explanation and test involved in the general theorem of the relation between radiation and absorption."

The value of Kirchhoff's experimental work is of the highest order, and is marked always by originality and precision; but it was as one of the small band of leaders in mathematical physics that his extraordinary powers were chiefly exerted. His University lectures, which were of the kind that constituted the glory of the German University system, represent an important part of his contributions to the progress of science. His lectures were quite unlike carefully thought out, well-arranged treatises, and can never be such. They were models of admirable processes of experiment and logical consequence. He seems to get rid of whatever

was indefinite, of every merely subjective judgment, of every customary phrase used without clearly defined meaning. In relation to such a subject, these statements characterize the matter and quality of thought much rather than mere style of composition. The progress of knowledge in mathematical physics, even more than in other branches of science, is essentially concerned with the recognition of how much in accepted statements of the results of observation is merely conventional and unnecessary. Here, more then elsewhere, precision of statement implies and generates precision of thought, and to rid the language of science of unmeaning or needless phrases is to advance knowledge.

For the last twenty years or so of his life Kirchhoff's health was much impaired, and his bodily activity interfered with by the results of a fall. He was seldom quite well afterwards, and for a long time he was able to get about only on crutches or in a wheel-chair.

His first wife died in 1869, leaving him two sons and two daughters. At Christmas, 1872, he married again. His second wife, who survives him, was Miss Louise Brömmel, at the time of her marriage Matron of the Ophthalmic Hospital at Heidelberg.

His death occurred peacefully, but not without warning, on the 17th October, 1887.

[The above notice is compiled from the eloquent oration delivered in memory of Kirchhoff by Professor Ludwig Boltzmann, of Graz, in November 1887; and from an article in the 'Deutsche Rundschau' for February 1888, by R. von Helmholtz.]

Coutts Trotter came up to Trinity College, Cambridge, from Harrow, at the age of eighteen, in the year 1855. He was elected a Scholar of the College at the earliest opportunity, and took his Degree in 1859, with honours both in Classics and Mathematics. He shortly afterwards became a Fellow of his College, and proceeded to Heidelberg to continue the study of Natural Science, which had interested him since the time when he listened to the Royal Institution Lectures of Faraday. While there he worked for some time at Physiology, under Helmholtz, and acquired considerable acquaintance with Botany and Chemistry. Soon after his return, he became Natural Sciences Lecturer at Trinity; and after that, though he delivered some lectures on Botany, he confined his attention mainly to Physics. He became a Member of our Society in 1879. The position of the Natural Sciences in Cambridge has changed

immensely in the last twenty-five years. The Honour Examinations, admitting to the degree of B.A., were first held in 1861, when three names appeared in the Class List; and in framing the lines along which the progress should take place, no man had so prominent a share as Trotter.

His wide acquaintance with literature, as well as with science, his great power of handling and arranging business details, his patient care and perseverance, his readiness to listen to his opponent's case, with his evident desire to reconcile in a fair and honest way conflicting claims, gave him an influence in the University which it will be difficult to replace; and by his death Scientific Research and Education in Cambridge has lost one of its ablest advocates. He did not contribute many papers to Scientific Journals or Societies. A few years since he communicated one to the Cambridge Philosophical Society (of which he was President at the time of his death), on Phenomena connected with the Melting of Ice. Another paper, containing the Results of Experiments on Ice at its Melting-point, carried out in the Ice Grotto at Gründelwald, was read before the Royal Society in 1886. Among his large and valuable collection of apparatus, which he left after his death to Newnham College, were some instruments ready packed for transit abroad in order to continue this research; but his illness prevented him from fulfilling his intention.

His name will live not through his scientific work, but in the statutes and regulations which govern University life, and which bear the impress of his wise judgment.

He had been seriously unwell during last winter and early spring; but in the summer he seemed almost to have regained his strength. When he returned from abroad in October, however, it was clear to his friends that there was too good cause for alarm; and an attack of inflammation of the lungs brought about the end on December 4th.

Thomas Samuel Humpidge was born at Gloucester, July 23rd, 1853. He was educated at the Crypt Grammar School, and in his fifteenth year entered a corn-merchant's office. Finding, however, that his tastes lay in the direction of scientific rather than commercial pursuits, he industriously gave all his leisure hours to study, and attended the local evening classes in connexion with the Science and Art Department. In 1873 he won the Silver Medal in Geology, and was awarded a Royal Scholarship at the Royal School of Mines.

He entered that Institution in 1874, and devoted himself chiefly to the study of Chemistry, under Professor Frankland. The year after he gained one of the Jodrell Scholarships, which enabled him in 1876 to proceed to the University of Heidelberg, where he studied under Professor Bunsen. In 1877 he passed the B.Sc. degree of the University of London, and in 1878 took his degree of Ph.D. (*summâ cum laude*). The same year he undertook teaching duties at the Fellenberg Institute at Hofwyl, near Berne, a post which he retained until appointed Professor of Natural Science in the University College of Wales, at Aberystwyth, in September 1879. Under the very cramped financial conditions of the Aberystwyth College at that date, the duties of Dr. Humpidge's Chair were truly exacting. Single-handed, he was expected to lecture on Chemistry, Physics, and Biology. After two years he was relieved of the last subject, and in 1884 of Physics. Nevertheless, whilst thus overweighted with teaching-work, he found time not only to organize on very slender means a fair Chemical Laboratory, but also to engage in research. All this proved a severe tax on his health and strength; and when, after the destruction of the College by fire in August 1885 (from which he narrowly escaped with his life), he redoubled his energies to organize the temporary laboratories, his weakened constitution sustained a shock from which it never recovered. While at Heidelberg he had specially studied the properties of the rare metals Yttrium and Erbium. At Aberystwyth he had devoted himself to a study of Beryllium, the atomic weight of which was at that time in doubt. This he redetermined: first, from its specific heat, and, secondly, from the vapour-density of its chloride and bromide. Finding the second method to produce results differing from those of the first method, he patiently repeated the calorimetric experiments, and had the satisfaction of proving that the specific heat of beryllium, like that of carbon, of boron, and of silicium, is abnormal at low temperatures, and only agrees with the law of Dulong and Petit as the temperature is raised. In the course of this research he constructed some new and elaborate calorimetric apparatus, with which he proposed to redetermine the specific heats not only of the rare elements, but of copper, tin, and other metals of which he had prepared specimens in a state of great purity. Unfortunately, not only these specimens, but the whole of his apparatus, as well as the manuscript records of many months of research, were destroyed in the College fire in 1885. Undaunted, he began again, reconstructed his apparatus, and prepared fresh

pure specimens for the calorimetric work. His health, however, broke down early in 1886; and he spent the autumn and the winter of 1886–87 in the south of Europe. At Easter, 1887, he returned to England, little fit for work, but apparently on the high road to recovery. Suddenly, in the autumn, cerebral deterioration set in, and he expired on November 30th, 1887. In addition to sundry memoirs and papers published in the 'Proceedings' and in the 'Philosophical Transactions' of the Royal Society, and in the 'Journal' of the Chemical Society, he published in 1884 a translation of Kolbe's 'Inorganic Chemistry.' He leaves a wife and two young children to mourn his loss.

The Society then proceeded to the election of Officers and Members of Council; and the new Council was constituted as follows:—

President.—Prof. A. W. Reinold, F.R.S.

Vice-Presidents who have filled the office of President.—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; Sir William Thomson, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, F.R.S.

Vice-Presidents.—Dr. E. Atkinson; Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; Prof. H. McLeod, F.R.S.

Secretaries.—Walter Baily, M.A.; Prof. John Perry, F.R.S.

Treasurer.—Prof. A. W. Rücker, F.R.S.

Demonstrator and Librarian.—C. Vernon Boys.

Other Members of Council.—Hon. R. Abercrombie; R. H. M. Bosanquet, M.A.; W. H. Coffin; Conrad W. Cooke; Prof. F. Fuller; W. N. Shaw, M.A.; A. Stroh; Prof. S. P. Thompson, D.Sc.; H. Tomlinson; G. M. Whipple.

Votes of thanks were passed to the Lords Committee of the Council on Education; to the Officers; and to the Auditors.

The Treasurer in Account with the Physical Society, from January 1st, 1887, to December 31st, 1887.

Dr.	£	*s.*	*d.*	£	*s.*	*d.*
Balance in Bank, January 1, 1887				352	14	10
Entrance-Fees	14	0	0			
Subscription for 1881	1	0	0			
Subscriptions for 1882	2	0	0			
„ 1883	5	0	0			
„ 1884	6	0	0			
„ 1885	16	0	0			
„ 1886	39	0	0			
„ 1887	135	0	0			
Excess Subscriptions	0	17	0			
Five Life Subscriptions	50	0	0			
				268	17	0
One year's Dividend on £400 Furness 4 per cent. Debenture Stock, less Income Tax	15	9	8			
One year's Dividend on £575 Midland 4 per cent. Preference Stock, less Income Tax	22	5	2			
One year's Dividend on £200 Lancaster Corporation Stock, less Income Tax	7	14	10			
One year's Dividend on £200 Metropolitan Board of Works Stock, less Income Tax	6	15	8			
				52	5	4
Received from Taylor and Francis :—						
Sales in 1886	14	0	0			
Sales in 1887	51	11	0			
				65	11	0
Balance due to Treasurer				3	12	3
				£743	0	5

Cr.	£	*s.*	*d.*	£	*s.*	*d.*
Balance due to Treasurer				3	7	8
Excess Subscriptions returned				0	17	0
Bank charges				0	3	9
Taylor and Francis :—						
Proceedings, vol. viii. (parts 1–4)	94	19	6			
Circulars, postage and addressing	20	2	0			
Members' separate copies	20	13	6			
Miscellaneous printing	22	10	9			
Joule, vol. i.	2	10	0			
„ vol. ii.	140	8	10			
				301	4	7
Gyde, for Binding				17	16	6
Haggard, for Binding				7	0	9
Index to Joule				15	0	0
Good, for Corporate Seal				2	11	0
Attendance at Meetings and incidental expenses				7	7	6
Invested in £254$\frac{7}{9}$ New South Wales 3$\frac{1}{2}$ per cent. Stock, with expenses				250	0	0
Petty Cash :—						
Dr. Atkinson				2	13	6
Prof. Reinold				1	14	8
Prof. Rücker				4	4	3
Balance in Bank				128	19	3
				£743	0	5

Audited and found correct,

London, January 20th, 1888.

GEORGE FULLER,
RICHARD INWARDS. } *Auditors.*

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, DECEMBER 31, 1887.

ASSETS.	£	s.	d.
Balance in Bank	128	19	3
Subscriptions due	88	0	0
£400 Furness 4 per cent. Debenture Stock	456	0	0
£575 Midland 4 per cent. Preference Stock	650	0	0
£200 Metropolitan Board of Works Stock	217	0	0
£200 Lancaster Corporation Stock	224	0	0
£254⅔ New South Wales 3½ per cent. Stock	249	7	5
	£2013	6	8

LIABILITIES.	£	s.	d.
Balance due to Treasurer	3	12	3
Bills outstanding:—			
Taylor and Francis (one Part of Proceedings)	57	18	10
Williams and Norgate	4	16	0
Balance	1946	19	7
	£2013	6	8

We have examined the above Account, and also the Securities at the Bank, and find the same to be correct.

London, January 20th, 1888.

GEORGE FULLER,
RICHARD INWARDS, } *Auditors.*